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Editor of the Proceedings:

CAPT. C. W. HUME, M.C., B.SC.

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PROCEEDINGS AT THE MEETINGS OF THE PHYSICAL SOCIETY

SESSION 1935–36

Except where the contrary is stated the meetings were held at the Imperial College of Science and Technology, South Kensington, the President being in the Chair.

October 4, 1935.

The President announced that the Council had elected the following to Student Membership of the Society: William Thomas Cowling, Eric P. George, Edgar Charles Woods.

The following presentations were acknowledged with thanks by the Joint Library Committee:

32 volumes of the *Philosophical Transactions of the Royal Society* (Series A) (1893–1914) by Miss M. D. Waller, B.Sc., F.Inst.P.

Volumes 76 and 77 (1934–5) of the *Transactions of the Institution of Naval Architects* by Dr Evelyn Shaw, C.V.O.

The following papers were read:

"Wood-water relationships, I. Molecular sorption and capillary retention of water by Sitka spruce wood," by W. W. BARKAS, M.Sc.

"A combined hydrogen and helium liquefier," by B. V. ROLLIN.

"Temperature-rise in a material of which the thermal properties vary with temperature," by J. H. AWBERY, B.A., B.Sc., F.Inst.P.

The following papers were read in title:

"The electron-oscillation characteristics of an experimental plane-electrode triode," by R. A. CHIPMAN, B.Sc., M.Eng.

"The conductivity of an orifice in the end of a pipe," by A. E. BATE, M.Sc., Ph.D., F.Inst.P.

"Absorption spectra of the chlorides and oxychlorides of sulphur," by R. K. ASUNDI and R. SAMUEL.

October 18, 1935.

The following were elected to the Fellowship of the Society: George Graham Harvey, Spencer Robert Humby, Michael Nelkon, Cecil Rowntree, John Berriman Smith.

The following presentation to the Joint Library was announced from the Chair as having been received since the last meeting; the thanks of the Society were accorded to the donor:

LODGE, Sir OLIVER. *My Philosophy*. Presented by the author.

The following papers were read:

"The effect of phase-change on the cochlea," by H. HARTRIDGE, M.D., F.R.S.

"The dependence of sensitivity of the selenium-sulphur rectifier photoelectric cell on the obliquity of the incident light, and a method of compensation therefor," by G. P. BARNARD, B.Sc., A.Inst.P.

"Thermochemical properties of nitrous oxide," by T. CARLTON-SUTTON, M.A., M.Sc., F.Inst.P., H. R. AMBLER, Ph.D., F.I.C. and G. WYN WILLIAMS.

The following papers were read in title:

"The integration of the glare effects from a number of glare sources," by B. H. CRAWFORD, M.Sc., A.Inst.P.

"The discrimination of the saturation of colours," by F. L. WARBURTON, A.R.C.S., D.I.C., M.Sc., A.Inst.P.

"Fine structure in the (^{2}D) series limit terms of the I^+ spectrum," by S. TOLANSKY, Ph.D., A.Inst.P.

"Absolute intensities in the spectrum of a low-pressure quartz mercury-vapour discharge burner," by A. J. MADDOCK, M.Sc., A.Inst.P.

November 1, 1935.

Christopher Locke Cook was elected to the Fellowship of the Society.

The President announced that the Council had elected Ernest Wallace Voice to Student Membership.

The following presentations to the Joint Library were announced from the Chair as having been received since the last meeting; the thanks of the Society were accorded to the donors:

LODGE, Sir OLIVER. *Beyond Physics*. Presented by the author.

SCHOFIELD, J. and SCHOFIELD, J. COLIN. *The Finishing of Wool Goods*. Presented by the authors.

The following papers were read:

"Experiments on conducting laminae in periodic magnetic fields," by J. MCGARVA BRUCKSHAW, M.Sc., Ph.D.

"An optical calibration problem," by T. SMITH, M.A., F.R.S.

"On the combination of observational data," by H. LEVY, M.A., B.Sc. and J. C. GASCOIGNE.

The following papers were read in title:

"The effect of crystal-size on lattice-dimensions," by G. I. FINCH, M.B.E., F.Inst.P. and S. FORDHAM.

"A determination of the specific heats of aqueous solutions of potassium chloride," by C. J. B. CLEWS, B.Sc., A.Inst.P.

"The thermomagnetic properties of nickel: II," by W. BAND, M.Sc. and Y. K. HSÜ, M.S.

"The longitudinal thermoelectric effect. VI: Mercury," by J. L. CH'EN, M.S. and W. BAND, M.Sc.

"Use of rotating parallel plane glass blocks for cinematography and projection with continuously moving films," by H. DENNIS TAYLOR.

November 15, 1935.

The following were elected to Fellowship of the Society: Leonard V. Chilton, K. R. Hope Johnston, R. W. Minter, C. E. Wynn-Williams.

The following papers were read:

"Dust figures formed by an electric spark," by A. E. BATE, M.Sc., Ph.D., F.Inst.P.

"Absolute measurement of the viscosity of liquid tin," by A. J. LEWIS, B.Sc., Ph.D.

"The measurement of very low relative humidities," by A. SIMONS, B.Sc.

The following papers were read in title:

"On the current-distribution in a loop aerial," by DENIS TAYLOR, M.Sc.

"A negative-resistance oscillator," by N. L. YATES-FISH, M.A., D.Phil.

December 6, 1935.

The following were elected to Fellowship of the Society: Frank Holliday, John Ashworth Ratcliffe.

The President announced that the Council had elected Kenneth Harold Waters to Student Membership of the Society.

The Thomas Young Oration was delivered by Prof. CHARLES FABRY of the Institut d'Optique, Paris, who took as his subject "La vision dans les instruments d'optique."

December 20, 1935.

The meeting was held in the Physics Department, University College, Gower Street, London, W.C. 1 by invitation of the Provost and Prof. E. N. da C. Andrade.

The laboratories of the department were open for inspection by members of the Society and their guests from 3.30 p.m. to 5 p.m. Various demonstrations were on view, mostly connected with problems of sound and vibration.

Introductory remarks on the general work of the Laboratory were made by Prof. E. N. da C. Andrade.

The following papers were read:

"The determination of viscosity by the oscillation of a vessel enclosing a fluid" (Part I), by E. N. DA C. ANDRADE, D.Sc., Ph.D., F.Inst.P., F.R.S. and Y. S. CHIONG, M.Sc.

"The determination of viscosity by the oscillation of a vessel enclosing a fluid" (Part II), by E. N. DA C. ANDRADE, D.Sc., Ph.D., F.Inst.P., F.R.S. and LEONARD ROTHERHAM, M.Sc.

"The determination of the viscosity of liquid gallium over an extended range of temperature," by K. E. SPELLS, Ph.D.

"The ripple method of measuring surface tension," by R. C. BROWN, Ph.D.

"A method of measuring the amplitude and damping of ripples," by R. C. BROWN, Ph.D.

"A method of investigating the Hall effect," by H. S. HATFIELD, Ph.D., F.Inst.P.

"The smoke method of measuring supersonic velocities," by R. C. PARKER, B.Sc.

January 7, 8, 9, 1936.

The Twenty-sixth Annual Exhibition of Scientific Instruments and Apparatus was held at the Imperial College of Science and Technology.

The following discourses were delivered:

"Some instruments used in recording sound on film," by R. A. BULL, B.Sc. (Eng.), A.M.I.E.E., of the Western Electric Company, Ltd.

"Electrical measurements before 1886," by R. W. PAUL, M.I.E.E., F.Inst.P.

January 24, 1936.

The President announced that the Council had elected the following to Student Membership of the Society: Percy George Forsyth, D. A. Jones, G. V. Stupart and Vincent Salmon.

A presentation was made to Mr T. Banfield.

The prizes and certificates awarded for the seventh competition in Craftsmanship and Draughtsmanship were presented.

The Presidential Address, entitled "Some reminiscences of scientific workers of the past generation, and their surroundings," was delivered by the Right Hon. Lord RAYLEIGH, M.A., Sc.D., LL.D., F.Inst.P., F.R.S.

The following papers were read in title:

"Some thermal and electrical aspects of the design of converters for the hydrogenation process," by A. BLACKIE, M.A., F.Inst.P., C. W. OCKELFORD and C. M. CAWLEY, Ph.D., M.Sc., A.R.C.S., D.I.C.

"Regularities in the spectrum of Iodine IV," by S. G. KRISHNAMURTY, M.A.

"The effect of dissolved air on the specific heat of water over the range 15° to 20° C.," by E. O. HERCUS, D.Sc., F.Inst.P.

"The ranges of α particles in photographic emulsions," by H. J. TAYLOR, M.Sc. and V. D. DABHOLKAR, M.Sc.

"The behaviour of a single-hair hygrometer under varying conditions of temperature and humidity," by W. G. Iles and Kathleen Worsnop.

"The β-ray spectra of some induced radioactive elements resulting from neutron bombardment," by R. Naidu, D.Sc. and R. E. Siday, B.Sc.

February 7, 1936.

The following were elected to the Fellowship of the Society: Henry Anthony Patrick Disney, Louis Essen, Frederick Hillman Gage, Ernest Pollard, Thomas Bertram Rymer, Henry Sessions Souttar, Alan George Gale Thomas, E. F. Forsyth, Herbert James Harold Starks (Transfer from Student Membership), Humphry Montague Smith (Transfer from Student Membership), Edward John Wenham (Transfer from Student Membership).

It was announced that the Council had elected Laurence William Walker to Student Membership of the Society.

The Thirteenth Duddell Medal was presented to Dr C. V. Drysdale, C.B., O.B.E., D.Sc., M.I.E.E., F.Inst.P.

The following papers were read:

"The viscosities of some liquid refrigerants," by J. H. Awbery, B.A., B.Sc., F.Inst.P. and Ezer Griffiths, D.Sc., F.Inst.P., F.R.S.

"The thermal and electrical conductivities of metals and alloys. Part II: Some heat-resistant alloys from 0° to 800° C.," by R. W. Powell, B.Sc.

The following papers were read in title:

"The properties of Heusler's alloy, and the true specific heat of manganese and its discontinuity," by J. R. Ashworth, D.Sc.

"The mechanical force on bodies of small susceptibility due to induced magnetization," by G. F. J. Temple, D.Sc., Ph.D., F.Inst.P.

A demonstration was given by Major C. E. S. Phillips, O.B.E., F.Inst.P., of "An experiment illustrating the support of a weight by a vertical tube containing sand, the lower end being covered by a thin membrane."

February 21, 1936.

The following were elected to the Fellowship of the Society: Ladislaus Kecskemeti, Donald McMillan, John Thomas Miller, Geoffrey William Warren, Roy Ratcliffe Williams.

The following papers were read:

"On a new type of electronic oscillator tube with parallel plane grids," by W. A. Leyshon, Ph.D., F.Inst.P.

"An experimental investigation of the validity of Ohm's law for metals at high current-densities," by H. M. Barlow.

The following papers were read in title:

"The relation between the apparent intensity of a beam of light and the angle at which the beam strikes the retina," by W. D. WRIGHT, D.Sc., A.R.C.S., D.I.C. and J. H. NELSON, B.Sc., A.R.C.S.

"The use of thermocouples for psychrometric purposes," by R. W. POWELL, B.Sc.

"Thermal diffusion in deuterium mixtures," by K. E. GREW, Ph.D. and B. E. ATKINS, B.Sc.

March 6, 1936.

The following were elected to the Fellowship of the Society: Alec Raymond Bennett, John Percival Vissing Madsen, Ronald Osmond Jenkins (Transfer from Student Membership).

The following papers were read:

"The accurate determination of ionospheric equivalent heights," by E. C. HALLIDAY, Ph.D.

"The variation of double refraction in celluloid with the amount of permanent stretch (*a*) at constant temperature, and (*b*) at different temperatures," by F. C. HARRIS, M.Sc., Ph.D. and B. R. SETH, M.A., Ph.D.

"A method of measuring secondary-electron emission from filaments," by L. R. G. TRELOAR, B.Sc.

The following papers were read in title:

"The thermal constants of setting concrete," by H. SHEARD, M.Sc.

"On the development of the quantum equation and a possible limit to its application," by H. T. FLINT, D.Sc.

"Note on the three absolute systems of electrical measurements," by the late Sir RICHARD GLAZEBROOK, F.R.S.

"The fourth unit of the Giorgi system of electrical units," by the late Sir RICHARD GLAZEBROOK, F.R.S.

March 20, 1936.

Annual General Meeting.

The Minutes of the previous Annual General Meeting were read and accepted as correct.

The reports of the Council and Hon. Treasurer were adopted.

The Officers and the Council for 1936–7 and the Auditors were elected.

Votes of thanks were accorded to the retiring Officers and Council and to the Governors of the Imperial College of Science and Technology.

Ordinary Meeting.

Vernon Ellis Cosslet was elected to the Fellowship of the Society.

It was announced that the Council had elected the following to Student Membership of the Society: Frederick James Bryant, Anson Quinton, John Bernard Warren.

The following papers were read:

"The relation between rate and arc for a free pendulum," by E. C. ATKINSON, M.A.

"On Airy's disturbance integrals and knife-edge supports for pendulums," by E. C. ATKINSON, M.A.

The following papers were read in title:

"Intensities in the principal series of lithium," by S. WEINTROUB, M.A.

"Electron energies and excitation in the helium positive column," by F. LLEWELLYN JONES, M.A., D.Phil.

"On absorption spectra and photodissociation of some inorganic molecules," by M. JAN-KHAN and R. SAMUEL.

The following demonstration was given by E. TYLER, D.Sc., F.Inst.P.: "Experiments with a new type of ripple tank."

April 3, 1936.

Arthur Warmisham was elected to the Fellowship of the Society.

The following presentation to the Joint Library was announced as having been received since the last meeting; the thanks of the Society were accorded to the donor:

BOUTRY, G. A. *Les Phénomènes Photoélectriques et leurs Applications.* Presented by the author.

The following papers were read:

"Wood-water relationships, II. The fibre saturation point of beech wood," by W. W. BARKAS, M.Sc.

"Time lag in photoelectric cells," by N. R. CAMPBELL, Sc.D., F.Inst.P., H. R. NOBLE and L. G. STOODLEY.

The following papers were read in title:

"Ultra-violet band systems of SiCl," by W. JEVONS, D.Sc., Ph.D., F.Inst.P.

"The size of atmospheric nuclei: some deductions from measurements of the number of charged and uncharged nuclei at Kew Observatory," by H. L. WRIGHT, M.A.

May 1, 1936.

It was announced that the Council had elected J. Stewart Marshall to Student Membership of the Society.

The following papers were read:

"The magnetic properties of manganese heated in nitrogen," by L. F. BATES, D.Sc., F.Inst.P., R. E. GIBBS, D.Sc., F.Inst.P. and D. V. REDDI PANTULU, M.Sc.

"Transmission of light through a pile of parallel plates," by R. A. HULL, B.A.

The following demonstrations were given:

"An experiment upon a method of increasing the rate of settlement of suspensions," by E. T. WILKINS, M.Sc., Ph.D.

"The method of assessing the extent and rate of settlement in suspensions and emulsions," by R. A. A. TAYLOR, A.R.C.S., M.Sc.

May 15, 1936.

It was announced that the Council had elected M. Akhtar to Student Membership of the Society.

The Twenty-first Guthrie Lecture was delivered by Prof. F. A. LINDEMANN, M.A., Ph.D., F.R.S., of the University of Oxford, who took as his subject "Physical Ultimates."

June 5, 1936.

The meeting was held in the Physics Department, Bedford College, Regent's Park, N.W. 1, by kind permission of Prof. W. Wilson. The Department was open from 3.30 p.m.

J. C. K. Rav was elected to the Fellowship of the Society.

The following papers were read:

"The mass of a convected field and Einstein's mass-energy law," by W. WILSON, D.Sc., Ph.D., F.R.S.

"Some experiments with neutrons having thermal energies," by J. R. TILLMAN, B.Sc., A.R.C.S.

"On the passage of neutrons through paraffin wax," by P. B. MOON, M.A., Ph.D.

"Notes on the neutrality of the neutron," by P. B. MOON, M.A., Ph.D.

The following papers were read in title:

"The structure of some metallic deposits on a copper single crystal as determined by electron-diffraction," by W. COCHRANE, Ph.D.

"The effect of an acoustically absorbent lining upon the sound-insulating value of a double partition," by J. E. R. CONSTABLE, M.A., Ph.D.

"An improved numerical method of two-dimensional Fourier synthesis for crystals," by H. LIPSON and C. A. BEEVERS.

June 19, 1936.

A visit to the Research Laboratories of the General Electric Company, Ltd. was arranged.

June 26, 1936.

The following were elected to Fellowship of the Society: Jessie Cattermole, James Chadwick, John Charles Wilson.

The following papers were read:

"The determination of absolute units," by NORMAN CAMPBELL, Sc.D., F.Inst.P.

"The density and coefficient of expansion of liquid gallium over a wide range of temperature," by W. H. HOATHER, M.Sc., A.Inst.P.

The following papers were read in title:

"The phenomenon of 'spreading' in the first positive bands of N_2," by E. T. S. APPLEYARD.

"The paramagnetism of the rare-earth sulphates at low temperatures," by L. C. JACKSON, M.Sc., Ph.D., A.Inst.P.

"The magnetic properties of amalgams," by L. F. BATES, D.Sc., Ph.D., F.Inst.P. and L. C. TAI, B.Sc.

"The magnetic properties of chromium," by L. F. BATES, D.Sc., Ph.D., F.Inst.P. and A. BAQI, M.Sc.

ADDENDUM to p. xvi of Vol. 47.

At the meeting held on June 21, 1935, the following were elected to the Fellowship of the Society: Gerald Thomas Prestoe Tarrant, Chintamani Ramchandra Dhodapkar, and Kwoh-Ting Li.

REPORT OF COUNCIL FOR THE YEAR ENDING FEBRUARY 29, 1936

MEETINGS

DURING the period under review 15 Ordinary Science Meetings were held at the Imperial College of Science and Technology. At these meetings 85 papers were presented, of which 56 were read in title. Seven demonstrations were given.

A Science Meeting was held on December 20, 1935, at University College by the kind invitation of the Provost and Professor E. N. da C. Andrade, F.R.S., and demonstrations were arranged in the laboratories of the Physics Department by the staff and research students.

The Thomas Young Oration was delivered by Professor Charles Fabry on December 6, the subject being "Vision in Optical Instruments."

The Presidential Address entitled "Some reminiscences of scientific workers of the past generation, and their surroundings" was delivered on January 24, 1936, by the Right Hon. Lord Rayleigh, M.A., Sc.D., D.Sc., LL.D., F.Inst.P., F.R.S.

SUMMER MEETING AT THE ROYAL HOLLOWAY COLLEGE, ENGLEFIELD GREEN, SURREY

A visit was paid on May 25 to the Royal Holloway College by kind invitation of the Principal, Miss E. C. Higgins, and Professor F. Horton, F.R.S. The science laboratories were visited and also the picture gallery, where members and their guests were entertained to tea.

On the return journey Eton College was visited. The party was kindly received by the Vice-Provost, Mr C. H. K. Marten, who gave an account of the history of the School.

THE DUDDELL MEDAL

The Twelfth Duddell Medal was presented to Dr W. Ewart Williams on March 15, 1935, for his work on interferometry.

The Council awarded the Thirteenth Duddell Medal to Dr C. V. Drysdale for his work in the design of electrical and optical instruments. The presentation was made on February 7, 1936.

ANNUAL EXHIBITION

The Twenty-sixth Annual Exhibition was held on January 7, 8, and 9, 1936, at the Imperial College of Science and Technology, by the courtesy of the Governing Body.

There were 84 exhibitors in the Trade Section and 29 in the Research and Experimental Section. The attendance during the three days was over 8500.

The following discourses were given:

"Some Instruments used in the Recording of Sound on Film," by R. A. Bull, B.Sc. (Eng.), A.M.I.E.E.

"Electrical Measurements before 1886," by Robert W. Paul, M.I.E.E., F.Inst.P.

PROGRESS REPORTS

The first volume of the series of Annual Progress Reports on Physics was issued in February, 1935, and a reprint was necessary.

The second volume is just published and is now on sale.

THE *PROCEEDINGS*

The table following shows the remarkable rate of growth of the volumes of the *Proceedings* and the corresponding increase in the membership of the Society:

Year	1924–5	1925–6	1926–7	1927–8	1928–9	1929–30	1931	1932	1933	1934	1935
Pages	355	494	472	349	605	606	643	624	854	914	1154
No. of Fellows	651	678	691	700	735	765	782	910	945	944	962

It is obvious that such a growth involves the Society in seriously increased printing expenses and Fellows communicating papers are earnestly requested to see that the text of the papers is as brief as is consistent with clarity.

REPRESENTATION ON OTHER BODIES

The three members who have represented the Physical Society on the British National Committee for Physics are Dr E. Griffiths, Mr T. Smith and Mr J. H. Awbery.

Professor Allan Ferguson, Dr D. Owen, Professor G. F. J. Temple and Mr J. H. Awbery have represented the Society on the Committee of Management of Science Abstracts.

Professor E. V. Appleton and Dr A. B. Wood have been representatives of the Society on the National Committee for Radio-Telegraphy.

Dr A. B. Wood and Dr E. Griffiths have represented the Society on the Board of the Institute of Physics.

OBITUARY

The Council records with deep regret the deaths of the following Fellows: Mr J. G. Bower, Sir Richard Glazebrook, Mr J. P. Kirkman, Sir John McLennan, Dr D. K. Morris.

MEMBERSHIP ROLL AT DEC. 31, 1935

	Total Dec. 31, 1934	Changes during 1935			Total Dec. 31, 1935
Honorary Fellows	11			–	11
Honorary Fellows (Optical Society)	8	Deceased		1	7
Ex-officio Fellows	4			–	4
Ordinary Fellows	921	Elected	56		
		Student transfers ...	4		
			60		
		Deceased	8		
		Resigned or lapsed ...	33		
			41		
		Net change		19	940
Students	67	Elected	28		
		Transferred to Fellow	4		
		Resigned or lapsed ...	7		
			11		
		Net increase		17	84
Total Membership	1011	Net increase		35	1046

REPORT OF THE HONORARY TREASURER

A moderate increase in the Society's income was outweighed by a large increase in the expenditure on its *Proceedings*, resulting in a deficit of £288. 8*s*. 1*d*. It is hoped that the steps which the Council is now taking will prevent such deficit next year. The publication of the first annual *Reports on Progress in Physics* has involved no charge on the general funds, the sum of £60 having been transferred from the special fund subscribed, to cover an estimated deficit.

The Society's investments have been valued at market prices on December 31st, 1935 through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank.

(Signed) ROBERT W. PAUL
Honorary Treasurer

February 25th, 1936

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1935

1934 £ s. d.	Expenditure	£ s. d.	£ s. d.
	To		
534 0 0	"Science Abstracts"		583 0 0
	Normal Publications:		
1877 9 1	"Proceedings" and Exhibition Catalogue	2299 17 0	
56 9 0	Notices	39 19 11	
222 12 8	Editorial and General Expenses	204 5 11	
			2544 2 10
	Special Publications:		
	Printing and Dispatching "Reports on Progress in Physics" (Vol. I)	574 2 7	
	Less Transfer from Special Reports Fund	60 0 0	
		514 2 7	
	Printing and Dispatching "Report of International Conference"	634 11 5	
106 12 10	*Printing and Dispatching "Report on Geometrical Optics"*		
			1148 14 0
272 16 9	Postage on Normal Publications and General Correspondence		350 15 2
34 4 4	Expenses at Meetings		32 19 0
10 12 6	Periodicals and Library		8 18 11
	Institute of Physics:		
500 0 0	Clerical Assistance and Office Expenses	528 16 0	
297 11 10	Electricity, Labour and Sundries in connexion with Exhibition	272 13 4	
			801 9 4
101 7 7	Sundry Expenses		92 3 9
	Honoraria to Lecturers		40 0 0
	Printing and Dispatching List of Members		49 7 1
95 7 10	*Balance, being excess of Income over Expenditure, carried forward to Accumulated Fund*		
£4109 4 5			£5651 10 1

1934 £ s. d.	Income	£ s. d.	£ s. d.
	By		
	Subscriptions:		
27 6 0	Entrance Fees	56 14 0	
1659 5 7	Fellows*	1654 18 10	
4 4 0	Voluntary†	4 4 0	
32 5 6	Students	39 13 6	
106 14 6	For "Science Abstracts" and Advance Proofs	109 0 9	
			1864 11 1
71 10 0	Transfer from Life Composition Fund of amounts paid by Fellows now deceased		30 0 0
825 14 6	Sales:		
	Normal Publications	955 11 2	
	Progress Reports (Vol. I)	514 11 10	
	International Conference Reports	569 11 11	
			2039 14 11
374 14 6	Advertisements in Publications		396 2 3
	Dividends from Investments	272 11 2	
247 19 0	*Less* Transfer to Duddell Memorial Fund	14 0 0	
			258 11 2
759 10 10	Exhibitors' and other Payments on account of Exhibition		774 2 7
	Balance, being excess of Expenditure over Income, carried forward to Accumulated Fund		288 8 1
£4109 4 5			£5651 10 1

* Eighty-seven Fellows paid reduced subscriptions by the arrangement with the Institute of Physics, the total rebate being £34. 13*s.* 6*d.*

† Voluntary subscriptions are subscriptions paid by Fellows who compounded for the low sum of £10.

BALANCE SHEET AS ON 31ST DECEMBER, 1935

BALANCE SHEET AS ON 31ST DECEMBER, 1935

LIABILITIES

	£ s. d.	£ s. d.	£ s. d.
Sundry Creditors		1623 19 2	
Life Compositions:			
As on December 31, 1934	1571 10 0		
Add Payment during year	21 0 0		
	1592 10 0		
Less Transfer to Income and Expenditure Account of amounts paid by Fellows now deceased	30 0 0		
		1562 10 0	
Subscriptions paid in advance:			
Members	35 13 2		
Publications	256 5 0		
		291 18 2	
			3478 7 4
TRUST FUNDS			
W. F. Stanley Trust Fund		336 0 0	
Duddell Memorial Trust Fund		446 12 9	
Optical Convention 1926, Trust Account		39 11 9	
"Special Reports on Physics" Account		83 1 0	
			905 5 6
GENERAL FUND			
Accumulated Fund:			
As on December 31, 1934		4071 8 10	
Less Decrease in value of Investments	237 0 0		
Less Balance of Income and Expenditure Account	288 8 1		
		525 8 1	
		3546 0 9	
A. W. Scott Bequest		185 19 6	
			3732 0 3
			£8115 13 1

ASSETS

	£ s. d.	£ s. d.	£ s. d.
Investments at Market Value on December 31, 1935:			
£1500 Consolidated Stock 2½%	1301 0 0		
£1000 War Loan 3½% Inscribed "A" Account	1060 0 0		
£750 War Loan 3½% Registered	795 0 0		
£650 Funding Loan 4%	760 0 0		
£500 India 3½% Stock	485 0 0		
£400 Lancaster Corporation 3%	392 0 0		
£399 London Midland and Scottish Railway 4% Debenture Stock	427 0 0		
£1000 London Midland and Scottish Railway 4% Preference Stock	820 0 0		
£500 London and North Eastern Railway 4% Debenture Stock	530 0 0		
£150 Southern Railway 5% Debenture Stock	198 0 0		
£300 Southern Railway Preferred Ordinary Stock	246 0 0		
£442 Southern Railway Deferred Ordinary Stock	90 0 0		
£400 War Loan 3½% Inscribed "B" Account	424 0 0		
		7528 0 0	
Dividends due from Investments		35 4 9	
Inland Revenue—Income Tax claimed for 1935		17 13 2	
Subscriptions due		26 12 0	
Sundry Debtors		149 5 6	
Cash at Bank: Current	347 2 6		
Cash in Hand	11 15 2		
		358 17 8	
		£8115 13 1	

Stock of publications on 31st December, 1935. At Honorary Treasurer's valuation . . . £1627 18 7

ROBERT W. PAUL, *Honorary Treasurer.*

We have audited the above Balance Sheet and have obtained all the information and explanations we have required. We have verified the Bank Balance and the Investments. In our opinion such Balance Sheet is properly drawn up so as to exhibit a true and correct view of the state of the Society's affairs according to the best of our information and the explanations given to us and as shown by the books of the Society.

SPENCER HOUSE, SOUTH PLACE, E.C. 2
25th February, 1936.

KNOX, CROPPER & CO.,
Chartered Accountants.

LIFE COMPOSITION FUND ON DECEMBER 31ST, 1935

	£	s.	d.
52 Fellows paid £10	520	0	0
1 Fellow paid £15	15	0	0
16 Fellows paid £21	336	0	0
1 Fellow paid £30	30	0	0
21 Fellows paid £31. 10*s.*	661	10	0
	£1562	10	0

W. F. STANLEY TRUST FUND

	£	s.	d.		£	s.	d.
Carried to Balance Sheet	336	0	0	£300 Southern Railway Preferred Ordinary Stock	246	0	0
				£442 Southern Railway Deferred Ordinary Stock	90	0	0
	£336	0	0		£336	0	0

DUDDELL MEMORIAL TRUST FUND

Capital

	£	s.	d.		£	s.	d.
Carried to Balance Sheet	424	0	0	£400 War Loan 3½% Inscribed "B" Account	424	0	0

Revenue

	£	s.	d.		£	s.	d.
Honorarium to Medallist	15	0	0	Balance on December 31st, 1934	23	12	9
Balance carried to Balance Sheet	22	12	9	Interest	14	0	0
	£37	12	9		£37	12	9

OPTICAL CONVENTION, 1926, TRUST ACCOUNT

	£	s.	d.		£	s.	d.
Balance carried to Balance Sheet	39	11	9	Balance on December 31st, 1934	37	0	0
				Sales of Publications	2	11	9
	£39	11	9		£39	11	9

A. W. SCOTT BEQUEST

	£	s.	d.		£	s.	d.
Expenses in connexion with Library	14	0	0	Balance on December 31st, 1934	199	19	6
Balance carried to Balance Sheet	185	19	6				
	£199	19	6		£199	19	6

"SPECIAL REPORTS ON PHYSICS" ACCOUNT

	£	s.	d.		£	s.	d.
Transfer to Income and Expenditure Account of estimated deficit on Progress Reports (Vol. I)	60	0	0	Balance on December 31st, 1934	142	10	0
				Donations during 1935		11	0
Balance carried to Balance Sheet	83	1	0				
	£143	1	0		£143	1	0

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 48, PART 1 *January* 1, 1936 NO. 264

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WOOD-WATER RELATIONSHIPS: (1) MOLECULAR SORPTION AND CAPILLARY RETENTION OF WATER BY SITKA SPRUCE WOOD

BY W. W. BARKAS, M.SC., Forest Products Research Laboratory, Princes Risborough, Aylesbury, Bucks.

Received June 3, 1935. *Read October* 4, 1935

ABSTRACT. An attempt is made to distinguish experimentally between the amount w_a of water held by molecular sorption, and that, w_c, held by capillary retention on finely ground flour of Sitka spruce wood. The method used consists in flooding the evacuated flour with an evacuated aqueous solution of sucrose and measuring the change in concentration of the solution with an interferometer. Since capillary retention requires for its manifestation free liquid surfaces in the interstices of the wood, it is claimed that, when the vacuum method here described is used, only true molecular sorption will cause a change in concentration of the solution. Since there are indications that a certain small amount of sucrose also is adsorbed by the wood, it is impossible to arrive at the exact value of w_a, but a minimum possible value $w_{a\,(\mathrm{min.})}$ is given which varies with the vapour pressure of the solution used, and amounts, on extrapolation to infinite dilution, to some 23 per cent of the dry weight of the wood. The difference between the total sorption W measured on the vapour-pressure isothermal and the values of $w_{a\,(\mathrm{min.})}$ here found is taken to represent the maximum possible value for w_c.

The question of the sorption of sucrose is discussed, and the suggestion is made that the moisture-content hysteresis in w_a is smaller than that in W; thus a greater proportion of water is held by capillary forces on desorption than on adsorption.

§ 1. INTRODUCTION

THE lowering of the vapour pressure of water held in wood can, in common with the same phenomenon in other gels, be accounted for either on the capillary theory, which holds that a low vapour pressure is due to the purely physical effect of the presence of curved menisci of the condensed phase in the small interstices of the solid phase, or alternatively on the assumption that molecular binding forces exist between the liquid molecules and those of the solid. The literature in support of each of these theories, or modifications of them, is vast, but the whole subject has been very fully discussed in McBain's *The Sorption of Gases and Vapours by Solids* (1932).

The present paper, which forms part of the work comprised in Project 8 of this Laboratory, is concerned with an attempt which was made to distinguish experimentally between these two theories as applied to the sorption of water by wood.

Previous works on wood-water relationships bearing on the question of sorption are not numerous. Pidgeon and Maass[1], Lavine and Gauger[2] and Seborg and Stamm[3] have measured the vapour-pressure isothermals of various woods in the form of small pieces or of fine flour and found the curves to be identical in shape, though not in numerical values, with those for cotton[4] and similar materials. Stamm and Loughborough[5] have made use of these curves in studying the thermodynamics of the swelling of wood. The work of Pidgeon and Maass has a direct bearing on the present discussion, since the authors conclude that molecular sorption accounts only for the low vapour-pressure values up to a moisture-content of about 2 per cent, before the hysteresis appears, and that the sorption in the hysteresis region is entirely capillary. They calculate from the Thomson equation[6] that the radius of the menisci at the lower end of this range is $4{\cdot}5 \times 10^{-8}$ cm. and that "near the saturation point" it is $3{\cdot}8 \times 10^{-6}$ cm.* Lavine and Gauger account for the differences between the vapour-pressure isothermals of various substances entirely in terms of the distribution of capillary magnitudes, while Stamm and Loughborough take the point of inflection on the isothermal as the approximate transition point between the two forms of sorption and say: "This relative vapour pressure gives a capillary radius...that is only 2·3 times the molecular diameter. This is very near the limiting distance expected for primary molecular attraction and should represent the limiting size of capillary in which capillary condensation can take place." Now it is evident that since the lower value calculated by Pidgeon and Maass is only twice the diameter of the hydrogen molecule and only half the narrow axis of the cellulose molecule[7], it is impossible to construct either a circular cavity of these dimensions surrounded by such large units, or a hemispherical water-surface inside it. The same difficulty applies almost equally to the calculation of Stamm and Loughborough. Since the derivation of the Thomson formula assumes a spherical meniscus, we must, for this reason alone, dismiss the quantitative validity of the calculation. This does not, however, rule out the capillary theory as a qualitative explanation of sorption at the higher vapour pressures because, though we may reasonably expect both the density and the surface tension of the water to be modified by its close association with the capillary wall[8], it is none the less true that a concave meniscus of any shape will result in a lowered vapour pressure, though its shape may be too complicated for mathematical computation. Another point in favour of the capillary theory is, as has been pointed out by Zsigmondy[9], that it very neatly explains the hysteresis between wetting and drying as being due to the fact that the delayed wetting of the capillary wall in the adsorption cycle results in a flattened meniscus and a higher vapour pressure. The true Thomson effect is observed only on desorption when the capillary walls are wet and the menisci hemispherical.

The argument leading up to the method used here to differentiate between moisture held by capillary forces and that held by molecular sorption is as follows. The capillary theory requires, for the manifestation of lowered vapour pressure, the

* Since at complete saturation these radii must be infinite, the authors presumably refer to the highest values of the vapour pressure which they actually measured.

presence of free water-surfaces, or more strictly air-water or vapour-water interfaces, in the interstices of the material, while the molecular theories will admit of a bond between the water and the wood even if no such interface exists—that is to say even when the wood is completely immersed in water. Hence any method which can demonstrate sorption when the wood is completely impregnated, without the possibility of free water-surfaces occurring, will be measuring molecular sorption and will ignore capillary retention. Since the total sorption at any vapour pressure is given by the vapour-pressure isothermal, any difference between this total and that proved to be molecular sorption may reasonably be put down to capillary forces. It should be noted that this method of distinction is purely experimental and does not require any assumption as to the nature of the molecular sorption nor the quantitative validity of the Thomson formula.

In the method adopted, samples of wood flour, ground sufficiently fine to ensure the cell structure being broken down, were evacuated till the dry weight was constant. This dry flour was then saturated in a vacuum with an aqueous sucrose solution of known concentration, which had also been evacuated as completely as possible. When the flour was completely immersed, the apparatus was opened to the air so that a pressure of 1 atmosphere forced the solution into the interstices of the wood wall. If molecular sorption occurred, water would be abstracted from the solution and held by the wood, thus leaving the solution at a slightly higher sugar-concentration than before. Capillary retention, on the other hand, would not be measured because no free menisci would be available for its manifestation. Thus if W is the total weight of water held by 1 g. of the wood as determined from the vapour-pressure isothermal, and w_a is the weight of water held by molecular sorption per gram of wood, then the difference is the weight w_c held by capillary forces, thus

W
w_a
w_c

$$W - w_a = w_c \qquad \text{.....(1).}$$

The present research, which was begun in 1931, was inspired by the work of Newton and Gortner[10] on the bound water in vegetable tissues. Their method showed the value of sucrose as an indicator of sorption, but they did not adopt a vacuum technique. This meant that the penetration of the material by the solution might be incomplete, free liquid surfaces might occur, and capillary retention might result by vapour diffusion from the solution across the air spaces. Their method was to measure the lowering of freezing-point of the solution and from it to calculate the amount of water abstracted, but this meant working at temperatures lower than those usually met with in practice, and with such quantities as would ensure a large change in concentration of the solution. Interferometer measurement of concentration-changes was therefore adopted, as it was suitable to any temperature, and concentration-changes as low as 0·01 per cent of sugar could be measured with reasonable accuracy. A report on the preliminary results of this work appeared in 1932[11], and the use both of sugar solution as an indicator and of the refractometer for measuring changes in concentration has been extended by others[12, 13, 14]; but so far as the author is aware no attempt has been made on the present lines to differentiate between molecular sorption and capillary retention.

§ 2. THEORY

M, C_1 Let X be the dry weight of flour, M the weight of solution added, C_1 the initial
C_2 concentration of sucrose solution in grams of sucrose per gram of solution, C_2 the
ΔC concentration of the solution after sorption, ΔC the change (C_2-C_1) in concen-
s tration, and s the weight of sugar held by molecular sorption per gram of wood.

Initially we have C_1M g. of sugar and $(1-C_1)\ M$ g. of water in the solution. After adsorption there are (C_1M-Xs) g. of sugar and $(1-C_1)\,(M-Xw_a)$ g. of water in the solution.

Therefore
$$C_2=\frac{C_1-Xs}{(1-C_1)\,M-Xw_a+C_1M-Xs},$$

so that
$$w_a=\frac{M\Delta C+Xs\,(1-C_2)}{C_2X} \qquad \text{.....(2).}$$

When the wood and sugar solution reach equilibrium, the aggregate (wood + sorbed water + sorbed sugar) must be in thermodynamic equilibrium with the remaining solution at its final concentration C_2; that is to say they must exert the same vapour pressure. Hence if s were known for different values of C_2, a vapour-pressure isothermal for w_a could be built up by using solutions of different concentrations whose vapour pressures may be obtained from tables. Now s is in fact unknown, but if it is assumed to be zero, equation (2) above shows w_a will
$w_{a\,(\mathrm{min.})}$ then have its minimum value which we may call $w_{a\,(\mathrm{min.})}$. Thus equation (2) may be written

$$w_a=w_{a\,(\mathrm{min.})}+s\,(1-C_2)/C_2 \qquad \text{.....(3),}$$

where $w_{a\,(\mathrm{min.})}=M\Delta C/C_2X$ and is the smallest possible value of w_a. The second term represents the amount to be added to $w_{a\,(\mathrm{min.})}$ to give the true molecular sorption if s were known. Thus w_a cannot be greater than $W-w_{a\,(\mathrm{min.})}$, and could be zero.

§ 3. MATERIALS

Blocks of Sitka spruce (*Picea Sitchensis* Carr.) were cross-cut and sifted to produce a fine sawdust whose mesh-size lay between 60 and 100. This was extracted for 48 hours at 20° C. distilled water with constant stirring, when on further shaking with distilled water the liquid showed no change in refractive index to the fifth place of decimals. The extractives removed in this way amounted to 0·75 per cent of the dry weight of the wood. After extraction the flour was air-dried without heat and stored in air-tight bottles. This method ensured a supply of material of great uniformity and was used for the whole of these experiments.

Pure analytical-reagent sucrose crystals, $C_{12}H_{22}O_{11}$, were used for the solutions, which were made up fresh to approximate strength as required. As soon as they had been prepared the solutions were put into the sorption apparatus K, figure 1, and evacuated till the residual air pressure, measured on a McLeod gauge, was less than 0·005 mm. of mercury. As freezing methods were not available, this evacuation was effected by evacuating a large vessel L, some 100 times the volume of the vessel containing the solution, and then putting L and K into communication.

In this way the pressure was reduced at each operation to about one hundredth of the difference between the pressures in the two vessels, whereas the loss of water was only the weight of vapour required to saturate the larger volume. Since the concentration of the solution was measured on a sample taken later in the experiment, this loss does not affect the results.

§ 4. APPARATUS

A sample of wood flour weighing about 1 g. was contained in each of the three bottles *A*, figure 1. These bottles, which had a capacity of about 25 cm^3, could be closed by the tap *B* and removed, while evacuated, at the ground-glass joint *C*, of which the inner half was connected to the bottle to facilitate the removal of the tap grease before weighing. The outer halves of the joints *C* were joined by *D* to the two-way tap *E*, one side of which led past a mercury manometer to the drying-tube *F*, which contained P_2O_5, and thence to the McLeod gauge and the Hyvac rotary pump. The other side of *E* (not shown) served to admit air when the bottles

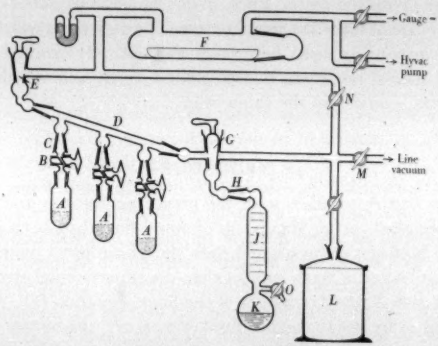

Figure 1. Diagram of apparatus.

had to be weighed. The other two-way tap *G* led down to a horizontal ground-glass joint *H* which held a graduated tube *J*, about 20 cm. long, on the end of which was a bulb *K* containing about 100 cm^3 of solution. The other branch of *G* led through the large vessel *L* to the tap *M*, and thence to drying tubes (not shown) and a service vacuum.

With *J* and *K* hanging down in the position shown, the solution could be evacuated first through *M* and later through *N* and *F* to the high vacuum in the manner described above, but when *J* was turned about the joint *H* through 180°, the solution ran down into *J*. With *E* and *B* closed, the tap *G* was opened to *D* which was thus completely filled with solution. By noting the level of the solution in *J*, any required volume could be admitted to the bottles *A*, the exact amount being determined by subsequent weighing.

The tube D was slightly inclined so that any minute bubbles would rise to the tap E and would not enter the bottles. These bubbles are at the pressure of the evacuated system, and do not represent poor evacuation of the apparatus. The small side-tube and tap at O, between J and K, served to admit air after the experiment.

A few points with regard to the bottles A require special notice. The bore of the holes in the taps was slightly enlarged at the ends so as to give a small space in which surplus tap grease could collect and not be drawn into the bottle by the rush of liquid on opening. The ground stoppers of the bottles had grooves round the lower ends of the ground surfaces and the grease was spread only above these grooves. In this way the surplus grease was enabled to squeeze into the grooves and could not mix with the solution in the bottles. The diameter of the bottles was such that when the stopper was replaced by a rubber cap the bottles themselves could be used as centrifuge tubes for separating out the flour from the solution.

It may be of interest to note that an accurate Rayleigh interference refractometer was constructed by using the tilt movement of a theodolite for mounting the compensating glasses. These, if 1 mm. thick, give a fringe movement of about $\frac{1}{10}$ of a fringe to 1 min. of arc of tilt of the compensator. The only parts which were specially bought for the instrument used here were the optically worked compensating-glasses and the special one-piece double-compartment cell for the liquids. The range covered was $\pm 0{\cdot}0017$ in the value of μ.

§ 5. PROCEDURE

The vacuum bottles together with the grease on the tap and the neck were evacuated and weighed. After about 1 g. of wood flour had been introduced into each bottle, the bottles were evacuated over the phosphorus pentoxide in F and weighed daily until a loss of water smaller than the experimental error, 0·2 mg., was registered. This gave X, the dry weight of the flour, equation (2). After prolonged evacuation to a pressure less than 0·005 mm. of mercury, the bottles were filled with solution and, as soon as the first one was detached, a sample of the solution was poured direct from the joint C into one of the two cells of the Rayleigh interference refractometer and a few drops were taken for the determination of the refractive index on the Abbé refractometer, which after temperature corrections gave the value of C_1 to 0·1 per cent from tables[15]. The necks of the bottles were flushed out and dried and the bottles were weighed to obtain M, the weight of solution. The small amount of solution held in the bore of the tap was negligible. The taps B were now opened so as to allow the atmospheric pressure to force the solution into the wood. In most of the experiments the bottles were completely filled with solution, so that if they were slowly rotated the flour and solution could be mixed without the introduction of air into the mixture. Experiment showed that the measured sorption was completed in less time than was necessary for manipulation (about 20 min.), and that the opening of the bottles to the atmosphere as described above did not affect the results, so that actually the atmospheric pressure is not

necessary for complete impregnation. Thus smaller quantities of solution could be used and the bottle could be shaken before being opened. With the more dilute solutions, the wood flour settled out in about half an hour and a sample of the supernatant liquid was then taken direct from the bottle to the other cell of the Rayleigh interferometer. With stronger solutions the sediment was centrifuged out, the bottle itself serving as centrifuge tube; thus errors due to evaporation were removed. The following tests were made to discover errors arising in the course of manipulation. (i) The use of empty bottles and distilled water showed that no detectable change in refractive index occurred as a result of solubility of the tap grease. (ii) The use of empty bottles and sugar solution also showed no detectable change in refractive index; this proved that evaporation losses, or sorption on the glass and the tap grease, were negligible. (iii) The use of wood flour and water showed that the extractives had been removed sufficiently well for the refractive-index change to be less than 0·00001.

The temperature of the apparatus was not regulated, but the solutions were shaken and centrifuged on the concrete floor of the laboratory, the temperature being usually between 19° and 20° C. and the maximum variations from 17·5° to 21° C.

§ 6. MEASUREMENT OF ΔC

After the two samples had stood in the interferometer for 2 hours, the difference $\Delta\mu$ between their refractive indices was measured to 0·00001 by taking the mean of the two values of $\Delta\mu$ given with the cells in the direct and reversed positions, the necessity for an exact determination of the zero of the instrument being thus removed. It was found that when the cells were left standing there was a tendency for concentration-gradients to be set up in them owing to moisture evaporating and condensing at the tops of the cells. Before a reading was taken, therefore, the cells were shaken to remix the solutions in each compartment. The correction in $\Delta\mu$ for the thickness of the walls of the empty cells amounted to 0·00012 and was applied to all readings. There was found to be no detectable error due to difference between the thicknesses of the cells themselves. $\Delta\mu$

The conversion of $\Delta\mu$ to ΔC could not be carried out directly since tables only give μ to 0·0001 and C in steps of 0·1 per cent, so differences of μ for 1-per-cent changes in concentration were taken and $\Delta C/\Delta\mu$ was plotted against the concentration at the centre of the range. In this way a large-scale graph of $dC/d\mu$ was obtained with very definite values from $C = 80$ per cent (in grams of sugar per gram of solution) to $C = 10$ per cent, while a less definite line could be traced to $C = 5$ per cent. It was found that Schönrock's tables[16] gave a much smoother curve than Main's tables[15], owing to slight differences in the fourth place of decimals, and they were, therefore, used for this purpose.

From this curve we have $(dC/d\mu)\,\Delta\mu = \Delta C$ while $C_1 + \Delta C$ gives C_2. The data necessary for the calculation of the $w_{a\,(\text{min.})}$ of equation (3) are thus completed.

§ 7. RESULTS

Since each concentration of sugar gives a different vapour pressure with which the wood + water + sugar aggregate must be in equilibrium, we may expect different values of $w_{a\,(\text{min.})}$ to be obtained for different concentrations, and this has proved to be the case.

Table 1

Reference	M/X	C_2	ΔC	$w_{a\,(\text{min.})}$	Relative vapour pressure of solution C_2	W at same relative vapour pressure
86/1	26·31	0·3533	+0·00233	0·175	0·9685	0·279
86/2	27·48		+0·00236	0·183		
88/14	28·58	0·2859	+0·00186	0·186	0·9775	0·296
88/16	29·03		+0·00182	0·186		
88/15	27·56		+0·00187	0·180		
98/13	54·55	0·1888	+0·00065	0·189	0·9872	0·325
98/11	51·9		+0·00071	0·195		
98/12	56·8		+0·00065	0·196		
82/13	25·22	0·1783	+0·00141	0·202	0·9882	0·339
82/11	25·21		+0·00141	0·200		
82/12	27·15		+0·00135	0·206		
100/4A	25·11	0·1029	+0·00086	0·215	0·9943	0·356
100/7	22·31		+0·00096	0·208		
100/9	24·52		+0·00086	0·210		
9/13	25·28	0·0988	+0·00079	0·2025	0·9945	0·357
9/12	26·02		+0·00077	0·2035		
92/4A	24·32	0·0554	+0·00049	0·214	0·997	0·370
92/7	24·26		+0·00049	0·2135		
92/9	23·79		+0·00049	0·2100		

In table 1 are given the results for each separate determination, grouped in sets representing separate runs of (usually) three bottles. The values of C_2 and ΔC are given as grams of sugar per gram of solution, while M/X is the weight-ratio of solution to wood flour. The last column gives the value of the equilibrium moisture-content for the same wood flour at the relative vapour pressure of the solution used, these values being taken from measurements of the vapour-pressure isothermal of Sitka spruce flour at 20° C., figure 4. A detailed description of the measurement of the isothermal will be given elsewhere, in a paper more concerned with its exact determinations[17], when the most reliable results are obtainable. It is sufficient to say here that the present figures for the moisture-content are unlikely to be in error by more than 2 per cent. The measurements were made on wood flour which had, as here, been previously evacuated to dryness.

§8. THE EFFECT OF THE INITIAL MOISTURE-CONTENT OF THE WOOD FLOUR

If the wood flour initially has a moisture-content m grams of water per gram of dry flour, equation (2) becomes

m.

$$w_a' = \frac{M\Delta C + Xs'(1-C_2)}{C_2 X} + \frac{m}{X}, \qquad w_a', s'$$

or

$$= w_{a\,(\text{min.})}' + \frac{s'(1-C_2)}{C_2} \qquad \ldots\ldots(4), \qquad w_{a\,(\text{min.})}'$$

where the dashes refer to the desorption process. Provided that the value of m is sufficiently high for the sign of ΔC to be reversed when the solution is mixed with the flour, desorption results and the solution becomes less concentrated.

A few experiments were made with flour having a known initial moisture-content above the minimum saturation value. After the dry weight of the flour had been obtained as before, the bulb K, figure 1, was filled with evacuated water. K was warmed and the bottles A were cooled, free distillation on to the flour being thus brought about. After m had been determined by weighing, the water was replaced by sucrose solution and the experiment proceeded as before.

Table 2 shows the values of $w_{a\,(\text{min.})}'$ so obtained.

Table 2

Reference	M/X	m	C_2	ΔC	Relative vapour pressure of C_2	$w_{a\,(\text{min.})}'$
102/1	49·9	0·717	0·3019	−0·00311	0·9735	0·203
102/2A	28·1	0·577	0·3011	−0·00385	0·9745	0·219
102/3	25·2	0·671	0·2993	−0·00566	0·9762	0·194
					Mean	0·205
104/4A	24·6	0·542	0·1615	−0·00209	0·990	0·223
104/7	24·4	0·516	0·1616	−0·00196	0·990	0·220
104/8	24·7	0·490	0·1617	−0·00189	0·990	0·202
					Mean	0·215

The mean values of $w_{a\,(\text{min.})}'$ are higher than the corresponding values of $w_{a\,(\text{min.})}$ for the dry flour, and this shows that a hysteresis in $w_{a\,(\text{min.})}$ occurs similar to that found in the isothermal itself, but owing to experimental difficulties there is considerably more scatter between the individual readings, which makes the true determination of $w_{a\,(\text{min.})}'$ less precise.

§9. DISCUSSION OF RESULTS

By extrapolating the values of $w_{a\,(\text{min.})}$ or $w_{a\,(\text{min.})}'$ to 100 per cent relative vapour pressure, it may be taken that the limiting value of either of these quantities is about 23 per cent of the dry weight of the wood, or rather more than half of the total sorption W in a saturated atmosphere. It is thus evident that the minimum

amount of water held in the wood by molecular sorption and not by capillary forces forms a larger proportion of the total sorption than that deduced by the authors previously mentioned[1,2,3]; and it must always be remembered that the actual proportion may be larger still if sugar sorption is present.

There is, however, a possible objection to the method used which may be raised, and it will be well to consider it here before dealing with the question of the sorption of sugar. It may be argued that the fine capillaries of the wood substance act as a filter to the solution, allowing the small water molecules to enter but being too fine to admit the larger sugar molecules. If this is so, then it is true that ΔC will be effected in the way and in the degree observed in these experiments. If, however, the effective radius of the sugar molecule in solution were known and were taken as the diameter of the smallest capillary which would admit sugar, it would be possible from the Thomson equation and the vapour-pressure isothermal to determine the moisture-content below which this filter action would operate. On the capillary theory, therefore, this moisture-content should correspond to the values of the so-called molecular sorption measured in these experiments. There is no precise information as to the dimension in question, but from the X-ray measurements of the crystallographic axes of sucrose we obtain a figure which will be larger than the sucrose molecule itself and which will therefore give too high a value for the moisture-content at which filter action could occur. Taking the largest axis of the sucrose molecule as $10{\cdot}6 \times 10^{-8}$ cm.[18], we obtain from the Thomson equation a vapour pressure corresponding to a moisture-content of only about 7 per cent. These experiments, on the other hand, show sorptions up to a moisture-content of 21 per cent with solutions of 97 per cent relative vapour pressure corresponding to a capillary radius of 360×10^{-8} cm. Thus the argument is untenable unless the molecular aggregation of sucrose in solution is more than 68 crystal units in diameter or about 165,000 in spherical volume. The number of molecules in the aggregate would have to be still greater in view of their smaller size.

A second possible argument is that the cellulose molecule in wood is generally considered to be of a long polar form grouped into bundles or micellae, and that water is attached to the side chains of these molecules. It may, therefore, be argued that the water is held not in cylindrical holes but in parallel-walled slits between one layer of molecules and the next, making the meniscus not spherical but cylindrical. Assuming the validity of the Thomson equation, and following the derivation of the formula given by v. Helmholtz[19], we can show that to exert a given vapour pressure the radius of such a cylindrical meniscus must be one half that of a spherical meniscus. This will still mean, however, that about 20,000 crystal units of sugar must be grouped if they are not to enter a pore giving a relative humidity of 97 per cent. This assumption of a cylindrical meniscus in a parallel-walled slit has the counterbalancing disadvantage that, at low vapour pressures, the calculated sizes are even smaller in relation to molecular dimensions, so that the theory becomes even less acceptable. Thus the only ground left for assuming that the effect here measured is due to a filter action must be that even at vapour pressures approaching saturation the value of the radius given by the Thomson

equation is some thirty-five times too small, whereas it is precisely at the higher vapour pressures that this equation becomes quantitatively acceptable.

§ 10. THE SORPTION OF SUGAR

If the true molecular sorption w_a of the water were known, the sorption s of sugar could be obtained by writing equation (3) thus

$$s = \frac{C_2\,(w_a - w_{a\,(\text{min.})})}{1 - C_2} \qquad \ldots\ldots(5).$$

As was pointed out above, w_a is not known but must lie between the value $w_{a\,(\text{min.})}$, which it has when s is zero, and W, the value found from the vapour-pressure isothermal. $w_a = W$ corresponds to the maximum value of s which we may call $s_{\text{max.}}$. $s_{\text{max.}}$

In table 3 the results shown in table 1 are again used to calculate the maximum

Table 3

Reference	C_2	$w_{a\,(\text{min.})}$	W	$s_{\text{max.}}$	Mean value of $s_{\text{max.}}$
86/1	0·3533	0·175	0·279	0·0568	0·0547
86/2		0·183		0·0525	
88/14	0·2859	0·186	0·296	0·0440	0·0448
88/16		0·186		0·0440	
88/15		0·180		0·0465	
98/13	0·1888	0·189	0·325	0·0319	0·0310
98/11		0·195		0·0303	
98/12		0·196		0·0308	
82/13	0·1783	0·202	0·339	0·0297	0·0299
82/11		0·200		0·0302	
82/12		0·206		0·0298	
100/4A	0·1029	0·215	0·356	0·0162	0·0166
100/7		0·208		0·0170	
100/9		0·210		0·0168	
90/13	0·0988	0·2025	0·357	0·0169	0·0168
90/12		0·2035		0·0168	
92/4A	0·0554	0·214	0·370	0·00913	0·0093
92/7		0·2135		0·00913	
92/9		0·2100		0·00938	

sorption of sugar, by assuming that $w_a = W$. Figure 2 gives graphically the relation of $s_{\text{max.}}$ to the concentration of the solution, showing that the mean values lie on an almost straight line which passes through the origin, as we should expect. This simple relation between $s_{\text{max.}}$ and C affords, however, no evidence that w_a is in fact equal to W, because a similar relationship would also hold if w_a were, at each vapour pressure, any simple fraction of W. The values of s would then be reduced in the same ratio.

Hitherto it has been tacitly assumed that the water and the sugar are sorbed independently, so that the water in the wood + water + sugar aggregate exerts a vapour pressure equal to that exerted by the same quantity of water in the simple case where only wood and water are present. To test the validity of this assumption

a sample of wood flour was flooded with distilled water in which sugar weighing 4 per cent of the dry weight of the flour had been dissolved. This was evaporated to dryness *in vacuo* without heat to give an intimate mixture of wood and sugar in

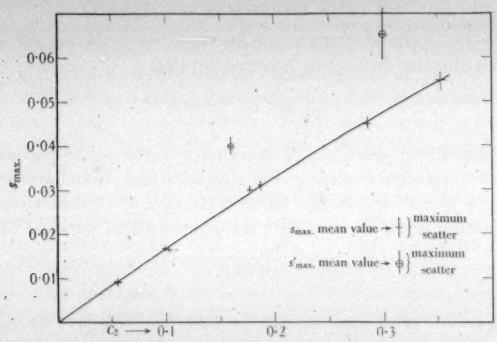

Figure 2. Curve relating $s_{max.}$ with C_2.

the above proportions. The isothermal of this mixture was determined simultaneously with that of a control sample of flour treated with distilled water only, so that differences between the moisture-contents of the two samples at the same

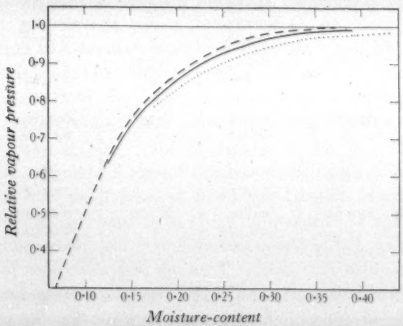

Figure 3. Adsorption isothermal of wood flour + 4 per cent of sucrose at 20° C. Wood flour only – – – – –; Wood + 4 per cent of sugar, experimental ———; Wood + 4 per cent of sugar, calculated · · · · · · · · ·.

vapour pressures might be accurately determined. In figure 3 the isothermal of the wood alone is shown as a broken line, based upon table 2, and that of wood + 4 per cent of sugar is shown as a full line. The dotted line shows the curve which would have been obtained had the wood and sugar each held its full complement of water independently. It is thus evident that the action of the sugar is not independent of that of the wood, and we may therefore conclude that (i) sugar is

sorbed by the wood, (ii) $w_a > w_{a\,(\mathrm{min.})}$, and (iii) the values of s shown in figure 2 are too large.

The isothermal of the ternary mixture shown in figure 3, while demonstrating the sorption of sugar, does not help in fixing the exact value of w_a because, as in the case where wood and water only are concerned, it is the total sorption by the wood and sugar that is measured, and no indication is given as to the proportion of this that is due to either the wood or the sugar separately.

When we make the attempt to get beyond the present position of knowing a minimum value for w_a and a maximum value for s the argument becomes much more speculative, but with this proviso a little more information may be gained from further study of the values of $w_{a\,(\mathrm{min.})}'$ found for desorption. Figure 4 shows the

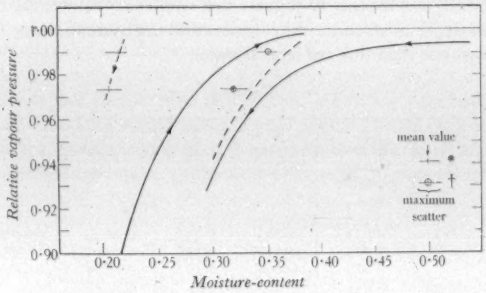

Figure 4. Adsorption and desorption isothermals of Sitka spruce flour at 20° C. * $w_{a\,(\mathrm{min.})}'$; † $w_{a\,(\mathrm{max.})}'$.

upper values of the isothermal both for adsorption and desorption. The latter values were measured on the same sample as the former, but the moisture-content was raised above the minimum saturation value by free distillation of water on to the flour till it exceeded 90 per cent. On drying by small steps a measurable drop in the vapour pressure occurred at moisture-contents much in excess of the adsorption-saturation value, showing that the hysteresis persists even at the saturation vapour pressure. The dotted line shows the commonly accepted shape of the hysteresis loop, which is usually obtained by extrapolation from lower desorption values and would probably be found on desorption from the fibre-saturation moisture-content of about 40 per cent.* This effect of hysteresis at saturation will be dealt with in a later publication[14], but it is important for the present discussion if the calculation of s' is to be attempted for the water-desorption cycle, since we are here starting from high moisture-contents. Table 2 showed that a hysteresis exists

* The term *fibre-saturation point* is defined to mean the moisture-content of wood when the cell wall is saturated but the cell spaces are empty. The point must correspond to the minimum moisture-content in equilibrium with a saturated atmosphere. Other work at this Laboratory(17) indicates that this equilibrium moisture-content is not a simply defined point and that further research is required. The fibre-saturation point is here taken provisionally as the moisture-content reached at 100 per cent relative vapour pressure in the *ad*sorption process, which for Sitka spruce flour is about 40 per cent at 20° C.

between $w_{a\,(\text{min.})}$ and $w_a'_{(\text{min.})}$, the wetting and drying values of the minimum molecular sorption. This hysteresis is not, however, necessarily due to differences in the sorption of water, since the measured values of $w_{a\,(\text{min.})}$ and $w_a'_{(\text{min.})}$ are affected by the sorption of sugar. Further, it is to be remembered that in the case of $s_{\text{max.}}$ the water and sugar are adsorbed simultaneously, whereas in that of $s'_{\text{max.}}$ the adsorption of sugar is coincident with the desorption of water because the wood had initially an artificially high moisture-content. This poisoning[20] of the surface by the previous sorption of water would lead one to expect that $s'_{\text{max.}}$ would be smaller, rather than greater, than $s_{\text{max.}}$ for a given final concentration C_2. If, however, we calculate $s'_{\text{max.}}$ from the values of W' shown in the desorption curve in figure 4, we obtain the values given in table 4, column 6, which are found to be greater than the corresponding values of $s_{\text{max.}}$ column 7, taken from figure 2. This is sufficiently improbable to suggest that whatever the ratio w_a/W, the corresponding ratio w_a'/W' is smaller; which means that the hysteresis loop for molecular sorption is narrower than that for total sorption.

Table 4

1 Reference	2 m	3 Relative vapour pressure of C_2	4 $w_a'_{(\text{min.})}$	5 W'	6 $s'_{\text{max.}}$	7 $s_{\text{max.}}$	8 $w_a'_{(\text{max.})}$ derived from $s_{\text{max.}}$
102/1	0·717	0·973	0·203	0·353	0·0648	0·0480	0·319
102/2A	0·577	0·974	0·219	0·356	0·0590	0·0477	0·332
102/3	0·671	0·976	0·194	0·361	0·0714	0·0475	0·305
	Means	0·974	—	—	0·0651	0·0477	0·319
104/4A	0·542	0·990	0·223	0·420	0·0380	0·0265	0·359
104/7	0·516	0·990	0·220	0·420	0·0393	0·0265	0·355
104/8	0·490	0·990	0·202	0·420	0·0421	0·0265	0·338
	Means	0·990	—	—	0·0398	0·0265	0·351

The shape of the desorption curve in figure 4 supports the view that, at artificially high moisture-contents, a large proportion of the water is held by capillary forces. To simplify the argument which follows we shall assume that the pores in the wood consist of circular holes of uniform cross-section but of varying sizes. There is actually no evidence to prove that this is so, but qualitatively the effect will be the same whatever the shape of the holes. Initially the wood contains in its interstices free water which, being in equilibrium with the saturated vapour pressure, must have flat surfaces. On evaporation of a small quantity of water these surfaces will at once become concave, giving the reduced vapour pressure corresponding to the drop in vapour pressure associated with a very small loss of water. This will occur on desorption whatever the initial moisture-content between the adsorption fibre-saturation point and complete saturation of the wood. The second stage commences when the radius of curvature of the menisci equals that of the largest pores in the wood. At this point the largest pores begin to empty, and since by the Thomson equation the rate at which the vapour pressure changes with curvature of meniscus is small for large capillaries, considerable loss of water

from the largest pores will be associated with only a small further drop in vapour pressure. This accounts for the shape of the desorption isothermal down to a moisture-content of about 40 per cent.

Hence there are good grounds for assuming that, on the desorption curve, at least all the water in excess of the adsorption fibre-saturation point is held by capillary forces, from which it follows that $w_a' < W'$ and that the values of $s'_{\max.}$ in table 4, column 6, are too high. If this reasoning is sound we may now deduce an upper limit for w_a', which we may call $w_a'_{(\max.)}$, from the improbability of the sugar adsorption being greater when water is initially present than when water and sugar are adsorbed simultaneously. These values are given in table 4, column 8, and are obtained by calculating $w_a'_{(\max.)}$ from equation (2), using the value of $s_{\max.}$ found from the adsorption experiments, column 7. The lower limit to w_a' remains equal to $w_a'_{(\min.)}$ as given in column 4. $w_a'_{(\min.)}$ and $w_a'_{(\max.)}$ are plotted in figure 4.

If more experiments had been made with previously moistened wood flour over a wider range of solution-concentrations C_2, the values of $w_a'_{(\max.)}$ could have been determined more accurately, but it hardly seems worth while to do this in view of the fact that the possible limits of w_a' are in any case fairly wide and the experimental difficulties considerable. The experiments here recorded are sufficient to show that the hysteresis loop in w_a is narrower than that in W, and that therefore more water is held by capillary forces on desorption than on adsorption.

§ 11. ACKNOWLEDGMENTS

In conclusion the author wishes to record his indebtedness to Prof. A. W. Porter, F.R.S., for his valuable criticisms of this work while it was in progress, to Mr W. A. Robertson, Director of the Forest Products Research Laboratory, for permission to publish the paper, and to the Chemistry Section of the Laboratory for its co-operation.

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APPENDIX ADDED OCTOBER 17, 1935

Measurements made on the unextracted flour of the same batch of Sitka spruce were not included in this paper, partly because the experimental difficulties were such as to lower one's confidence in the accuracy of the results, but chiefly because an accurate isothermal for the natural wood was not available when the paper was submitted. Since then I have found that the isothermal of natural white spruce has recently been measured by Filby and Maass, and as this curve agrees well with my less accurate measurements on natural Sitka spruce I think it may serve as a basis of calculation.

Before the calculation of w_a can be made for natural wood, a correction has to be applied for the refractive index of the cold water extractives which will dissolve in the sugar solution. This was done by first comparing with pure water the refractive index of the flour-water mixture and then making sure that the change of refractive index due to the extractives was the same in pure water as in a sugar solution. For the first test different proportions of flour and water were shaken together *in vacuo* for different times. It was thus shown that, for the range of flour-solution ratios used in the experiments to be described, the extractives were completely dissolved in about 2 hours and gave a refractive-index change equivalent to 0·00160 for 1 g. of flour per 1 g. of water. Hence the correction for any flour-water ratio could be calculated. For the second test, samples of the solution of the extractives which had been removed from the flour used in the main experiments, page 4, were mixed in equal volumetric proportions with (*a*) pure water, (*b*) 8-per-cent sugar solution, and (*c*) 19-per-cent sugar solution. It was found that the refractive-index change was sensibly equal in each case so that the refractive index due to the extractives was volumetrically additive to that of the sugar solution.

Table 5 gives the results in the same way as does table 2 in the main paper, page 9, with the addition of W from the isothermal and the calculated values of $s_{\max.}$ as in table 3, page 11.

If $s_{\max.}$ is plotted against C_2 it will be found that the means of the points for s for dry flour lie almost exactly on the line shown in figure 2, except in the case of the most concentrated solution, while for the flour with a high initial moisture-content the means of s' lie at values roughly corresponding to those for s' in figure 2 but, as in the case of the extracted flour, the scatter is considerable owing to experimental difficulties. For s' also the points for the highest concentration are high compared with the values shown in figure 2, but the necessity of correcting for the refractive index of the extractives considerably increases the possibility of experimental error, so it is possible that this observation is due to pure coincidence.

In general we may conclude that for the natural wood the results are almost identical with those for extracted wood, and therefore that the proportions of water held by molecular sorption are identical. This is borne out by the fact that the isothermals are also practically identical in each case.

Table 5

Reference	M/X	m	C_2	ΔC	Relative vapour pressure of C_2	$w_{a\,(\min.)}$	W	$s_{\max.}$
				(*a*) Dry flour				
116/13	24·91	Zero	0·3938	0·00277	0·962	0·175	0·291	0·0754
116/11	26·41	,,	0·3938	0·00281		0·189		0·0662
116/12	25·50	,,	0·3937	0·00269		0·174		0·0760
70/4A	28·38	,,	0·1973	0·00148	0·986	0·213	0·330	0·0288
70/7	23·53	,,	0·1971	0·00171		0·204		0·0306
70/8	22·27	,,	0·1971	0·00167		0·189		0·0346
76/1	23·31	,,	0·1940	0·00169	0·987	0·204	0·331	0·0306
76/2A	26·32	,,	0·1942	0·00148		0·201		0·0314
76/3	22·69	,,	0·1940	0·00169		0·197		0·0323
56/4	11·97	,,	0·1676	0·00302	0·989	0·217	0·350	0·0268
56/5	12·23	,,	0·1675	0·00307		0·225		0·0252
56/9	12·32	,,	0·1679	0·00272		0·202		0·0299
				(*b*) Wet flour				
						$w'_{a\,(\min.)}$		$s'_{\max.}$
114/16	26·7	0·520	0·3832	−0·00476	0·963	0·193	0·339	0·0907
114/15	25·9	0·453	0·3839	−0·00409		0·187		0·0947
106/14	22·7	0·614	0·3578	−0·00638	0·968	0·200	0·344	0·0804
106/16	25·7	0·481	0·3570	−0·00403		0·191		0·0882
106/15	28·2	0·414	0·3581	−0·00308		0·208		0·0808
108/13	12·14	0·405	0·1873	−0·00314	0·987	0·200	0·402	0·0465
108/11	33·2	0·543	0·1890	−0·00206		0·208		0·0455
108/12	25·5	0·577	0·1888	−0·00231		0·236		0·0387

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A COMBINED HYDROGEN AND HELIUM LIQUEFIER

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Communicated by Prof. F. Simon, May 28, 1935. *Read October* 4, 1935

ABSTRACT. A description is given of a helium liquefier which needs only liquid air for the initial cooling and is designed to enable low-temperature experiments to be made in the ordinary laboratory.

§ 1. INTRODUCTION

Recent developments in low-temperature technique have made it possible to work at liquid-helium temperatures in any laboratory in which liquid hydrogen is available. However, as in many laboratories a supply of liquid hydrogen is unobtainable it seemed useful to design an apparatus in which only liquid air is required for the preliminary cooling and in which a small quantity of hydrogen, sufficient to obtain the necessary starting-temperature for the helium stage, is liquefied inside the apparatus itself. For occasional work it is simpler and much less expensive to construct a double liquefier of this type than to set up separate liquefiers for hydrogen and helium.

In the apparatus described here there is first a small Linde liquefier for hydrogen of the type described by Ruhemann[1]. For the helium stage the expansion method developed by Simon[2] is employed.*

The hydrogen liquefier is worked from high-pressure hydrogen cylinders so that no compressor is needed. For the helium liquefier a small compressor is used, but for occasional work this is not necessary as it would be quite possible to work with a high-pressure helium cylinder.

It was thought worth while to give a complete description of the apparatus and technique so that the important details in the construction and operation could be more easily reproduced.

§ 2. GENERAL DESCRIPTION OF THE APPARATUS

To illustrate the principle of the methods employed a simplified diagram of the liquefier is shown in figure 1 together with connexions to the hydrogen and helium circuits.

With the exception of the glass Dewar vessel *D* the apparatus is made entirely of metal and the various parts are soldered together.

* The possibility of constructing such a double liquefier was first shown by preliminary work by Kaischev(3) in Prof. Simon's laboratory.

The liquid-hydrogen vessel A and the helium vessel C are suspended in an enclosure E_1 which is surrounded on the outside by liquid air contained in the Dewar vessel D. The temperature of the liquid air can be reduced below its normal boiling-point by pumping off through the outlet tube q. When the whole apparatus has reached the lowest temperature obtainable with liquid air, the enclosure E_1 is evacuated with a high vacuum pump.

High-pressure hydrogen enters the apparatus by the tube a and passes through the liquid air and the heat-exchangers to the expansion valve V where it ultimately liquefies, and the liquid drops into the vessel A. The outgoing gas passes out through the exchangers, so cooling the incoming gas. The gas leaves the apparatus by the tube b and passes ultimately through the flow-meter F_1 so that the rate of flow of gas can be measured.

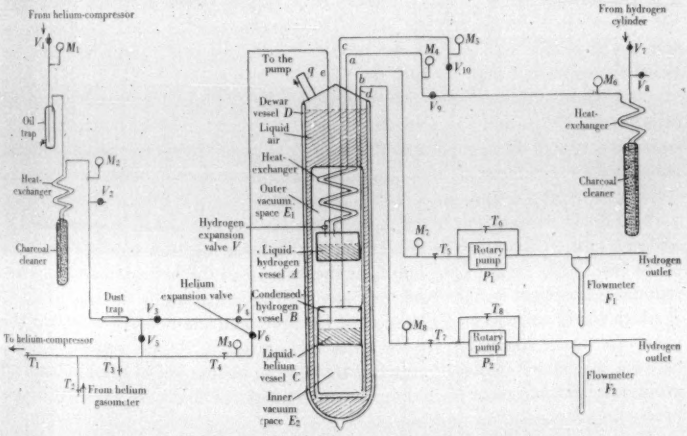

Figure 1. Simplified diagram of helium liquefier and external apparatus.

The vessel C is filled with helium gas maintained at a pressure of 130 atmospheres. In order to cool this gas further, liquid hydrogen is condensed in the vessel B by admitting hydrogen gas to the tube c so that it passes first through the liquid air and then through the liquid hydrogen in A, where it is condensed, and the liquid drops down into B.

When B is filled with liquid hydrogen at 20° K. the hydrogen inlet valve V_{10} is closed and the temperature of B and C is further reduced by pumping off through the outlet tube d by means of the pump P_2. In this way the temperature can be lowered to about 11° K., below the triple point, 14° K. of hydrogen. During the whole of the cooling process, the helium vessel C is connected to the high-pressure helium supply. Ultimately nearly all the hydrogen in B is evaporated and C contains helium at a pressure of 130 atmospheres and a temperature of 11° K.

The helium inlet valve V_4 is then shut and the valve V_6 is opened slowly so that the helium in C is expanded. This adiabatic expansion process gives rise to a considerable cooling, and eventually the helium liquefies in C. At the conclusion of the expansion, C is filled about two-thirds full with liquid helium at 4·2° K. The apparatus on which measurements are to be made is situated in the inner enclosure E_2.

§ 3. COMPLETE DESCRIPTION OF THE APPARATUS

A complete diagram of the liquefier is given in figure 2, which is drawn to scale with the exception of the connecting tubes.

The apparatus is suspended from the upper brass cap J by the connecting tubes. The Dewar vessel D is joined to the cap by a rubber sleeve T with a packing of felt F between the metal and the glass. The Dewar vessel is filled with liquid air and can be pumped off through the tube q. Liquid air can be siphoned into the vessel from a storage flask through the tube m.

On account of the extremely low vaporization heat of liquid hydrogen and liquid helium (roughly $\frac{1}{10}$ and $\frac{1}{100}$ respectively of the value for oxygen per cm^3), it is essential to design the apparatus so that heat-conduction between parts at different temperatures is reduced to a minimum. Thus all connecting tubes are made of German silver and are as long and thin as possible.

The outer vacuum enclosure E_1 consists of the cylindrical copper case Y_1 soldered to the copper cap k_1 and similarly the inner vacuum enclosure consists of the case Y_2 soldered to the ring k_2 at the bottom of the helium vessel C. Surrounding the helium vessel C and the inner vacuum enclosure is the copper shield R which serves to prevent conduction of heat between the helium vessel and the outer case by the residual gas in the outer vacuum space. Direct heat-conduction between the parts at liquid-air temperature and the helium vessel must be entirely avoided, so all tubes must be in thermal contact with the hydrogen vessel A before proceeding to the helium vessel.

High-pressure hydrogen comes in by the copper tube a and passes through the inner tube of the exchanger X_1 through the copper spiral S_1, immersed in liquid air, through the inner tube of the exchanger X_2 in the outer enclosure E_2, and so to the expansion valve V. The expansion valve may be adjusted by means of the external handle H. On leaving the vessel A the cold hydrogen gas passes through the outer German-silver tube of the exchangers X_2 and X_1, and when it leaves the apparatus by the tube b it is almost at room-temperature.

The inlet for the hydrogen which is to be condensed is at c. The gas is first cooled to liquid-air temperature in the copper spiral S_2 and then passes through the copper spiral S_3 in the liquid hydrogen vessel A, where it condenses and runs down into the vessel B. The vessel B is provided with the outlet tube d so that a flow of gas can be passed through B.

High-pressure helium is led in by the tube e and is cooled to liquid-air temperature in the copper spiral S_4 and to liquid-hydrogen temperature in S_5. It then

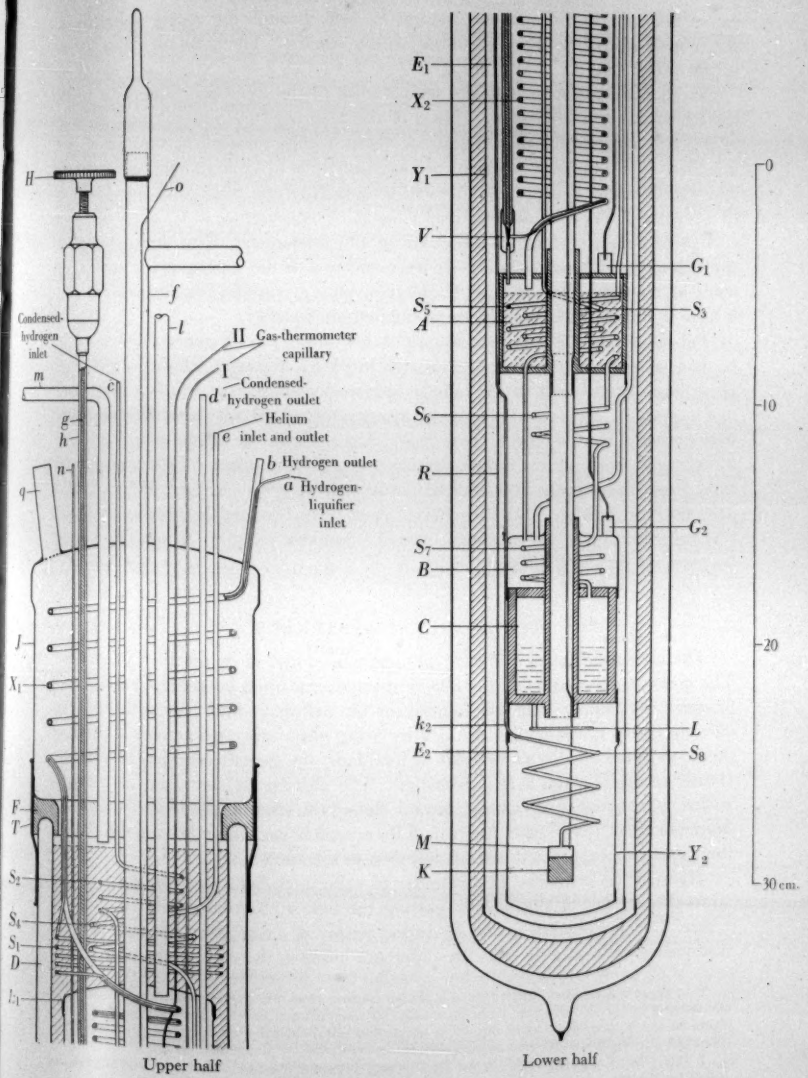

Figure 2. Complete diagram of liquefier.

passes through the German-silver spiral S_6, and through the copper spiral S_7 in the condensed-hydrogen vessel, to the helium vessel C. The same tube also serves as the outlet tube.

To indicate approximately the temperature of the hydrogen-liquefier a small gas thermometer is employed. This is of the type used by Simon[2] and consists of a brass vessel G_1, with a volume of about 1 cm^3, soldered to the top of the liquefier. It is connected by means of a capillary tube to a diai vacuum manometer. The thermometer is evacuated at room-temperature and filled with pure helium to a pressure of about 1 atmosphere. Change of temperature of G_1 gives rise to a change of pressure which is indicated on the manometer. The thermometer is conveniently calibrated at liquid-air temperature and the boiling-point and triple point of hydrogen, 20° and 14° K. respectively. A similar gas thermometer G_2 is used to indicate the temperature of the helium-liquefier.

For simplicity the specimen on which low-temperature measurements are to be made is shown in the diagram as a solid block K. The most satisfactory method of cooling the specimen is generally to use condensed helium which is contained in the vessel M. The helium is admitted at a pressure of 2 atmospheres (1 atmosphere over-pressure) *via* the tube n. It is cooled first to liquid-air temperature and then to hydrogen temperature, and on passing the helium-liquefier C it condenses and runs down through the thin-walled German-silver spiral S_8 into M.* A shield prevents heat radiation from the external parts from reaching the specimen. If the thermal insulation of the specimen is good a temperature of 1° K. can be reached by pumping off the condensed helium.

§ 4. EXTERNAL APPARATUS

The helium necessary for the experiments is stored in an oil-filled gasometer. The pressures necessary for the experiments are obtained by using a small compressor. On coming from the compressor the helium is first passed through an oil-trap, figure 1, and is then purified by being passed through activated charcoal cooled in liquid air. To avoid waste of liquid air, the gas entering and leaving the cleaner passes through a heat-exchanger. The charcoal is contained in a thick-walled metal cylinder of volume 300 cm^3. Before the starting of an experiment it is heated to about 300° C. and pumped off for several hours. After leaving the cleaner the gas passes through a dust-trap and then to the apparatus.

Hydrogen is contained in a cylinder of volume 50 litres at a pressure of 200 atmospheres† and is purified by passing through a charcoal cleaner of volume 1 litre. The flow-meters F_1 and F_2 consist simply of a capillary tube with a water manometer indicating the pressure-difference between the ends of the tube.

* In figure 2 a capillary outlet tube o is shown coming from the helium condensation vessel M and passing up the central tube of the apparatus. It was included to assist the condensation of the liquid helium by allowing a small amount of gas to flow out during the condensation process. It has recently been found that its presence is probably not essential for the condensation.

† It is, however, quite possible to use the ordinary storage cylinders of volume 25 litres at pressure 120 atmospheres.

The glass apparatus is not shown in the diagram. It consists of two mercury condensation pumps for pumping the vacuum spaces and the condensed helium, with liquid-air traps and discharge tubes. The pumps are heated by electric furnaces as it is of course very undesirable to have flames near an apparatus using hydrogen. There are two flasks of volume 3 and 5 litres respectively which can be exhausted by the pumps and filled with pure helium from the helium circuit. This helium is admitted to the vacuum spaces to give thermal exchange when desired, and is used also as a supply of helium for condensation in the vessel M. There is also a mercury manometer for measuring the vapour pressure of the helium condensed in M.

§ 5. DIMENSIONS OF THE APPARATUS AND CONSTRUCTIONAL DETAILS

As it is impossible to show the dimensions completely in a diagram the more important details are given here. The hydrogen vessel A is turned from solid copper and has a wall thickness of 2 mm. The spirals S_3 and S_5 are of copper tube having an external diameter of $\frac{3}{16}$ in. and a wall thickness of $\frac{1}{32}$ in. After the spirals have been mounted in the vessel A the flat annular top is placed in position and silver-soldered in. The volume of the vessel is 75 cm.³ The helium vessel C is turned from solid phosphor-bronze, though copper could be used equally well. The external walls have a thickness of 4 mm. and the internal walls 2 mm. The annular top is silver-soldered in. The spiral S_7 is of $\frac{3}{16}$-in. copper tube. The vessel B is beaten out of copper sheet and soft-soldered to C. Further details of the tubes are given in the following table:

Tube	Material	External diameter	Wall-thickness
f	German silver	1 cm.	0·1 mm.
S_6	,, ,,	4 mm.	0·5 mm.
S_2	Copper	$\frac{3}{16}$ in.	$\frac{1}{32}$ in.
S_4	,,	$\frac{1}{4}$ in.	$\frac{1}{32}$ in.
S_1	,,	2·5 mm.	0·5 mm.
S_8	German silver	2·0 mm.	0·1 mm.
e	,, ,,	4 mm.	0·5 mm.
d*	,, ,,	4 mm.	0·2 mm.
n†	,, ,,	4 mm.	0·2 mm.
c	,, ,,	2 mm.	0·2 mm.
b	,, ,,	8 mm.	0·1 mm.
G_1, G_2	,, ,,	0·7 mm.	0·2 mm.
X_1‡	,, ,,	5 mm.	0·5 mm.
X_2‡	,, ,,	4 mm.	0·3 mm.

* The portion of d adjacent to the hydrogen vessel A is of $\frac{3}{16}$-in. copper tubing and is soldered to A.

† The portions of n passing the vessels A and C and soldered thereto are of $\frac{3}{16}$-in. copper tubing.

‡ The internal tubes of X_1 and X_2 are of copper, diameter 2·5 mm. and wall-thickness 0·5 mm.

The exchangers are constructed by placing one tube inside the other and then winding the two tubes into the spiral form. The valve V is turned from solid brass and the spindle is of solid steel of diameter 3 mm. The outer tube h which has to

support the high pressure is of German silver with a diameter of 6 mm. and wall-thickness of 1·0 mm. The construction of the valve at the upper end of the spindle is similar to that of the ordinary high-pressure valve. The valve is made tight with a packing consisting of a mixture of graphite and lead. In the external hydrogen and helium circuits the tubes used for the high pressure are of copper, with a diameter of $\frac{1}{4}$ in. or $\frac{3}{16}$ in. and a wall-thickness of $\frac{1}{32}$ in. For the low-pressure circuit, tubes of composition alloy having an internal diameter of $\frac{1}{2}$ in. are employed.

In the construction of the apparatus each part is tested in turn for strength and absence of leaks with hydrogen gas at suitable pressure.

When the vessels A and B have been constructed and tested they are mounted on the central tube f, the caps k and J are assembled on the tube, and the connecting tubes and spirals are then soldered in position. Soft solder has been used for nearly all the joints.

When the apparatus has been completed it is rigidly clamped by the upper cap J and the various connexions are made to the hydrogen circuit, the helium circuit and the glass apparatus. The upper end of the central tube f is closed with a glass tube p. All glass-metal joints are made with vacuum wax and all such joints are kept as far away as possible from the liquefier so that they may not crack during the cooling of the liquefier.

The case Y_2 of the enclosure E_2 is soldered to the ring k_2 with Wood's metal, and similarly the screen R is soldered to the hydrogen vessel A, and the case Y_1 is soldered to the cap k_1, Wood's metal being used. When changes have to be made in the experimental apparatus in the enclosure E_2 it is only necessary to unsolder these three Wood's-metal joints.

As copper sheet is often not vacuum-tight, all large metal surfaces, such as the vacuum cases Y_1 and Y_2, are covered with a thin layer of tin solder.

§ 6. OPERATION OF THE LIQUEFIER

A description is given here of the operation of the liquefier during a typical experiment. When the hydrogen and helium cleaners have been heated and pumped out for 1 or 2 hours they are cooled in liquid air and filled with compressed hydrogen and helium respectively. The hydrogen vessels A and B in the liquefier are pumped out and filled with pure hydrogen to a pressure of 2 or 3 atmospheres. The helium vessel C is pumped out and filled with compressed helium. The vacuum spaces E_1 and E_2 and the helium condensation space M are exhausted. The glass apparatus is pumped out and the 5-litre flask is filled with pure helium to a pressure of 2 atmospheres. The readings of the gas thermometers are taken. The cooling is now started and the following sequence of operations is carried out.

0 hr. The Dewar vessel D containing liquid air* is put on the apparatus. Helium gas is now admitted to the enclosures E_1 and E_2 to a pressure of about 1 cm. This gives thermal exchange between the inner parts and the outer case.

0 hr. 40 min. The Dewar vessel is pumped.

* Liquid oxygen is generally used in this laboratory, but liquid air or nitrogen would be preferable if they were available.

1 hr. 15 min. The whole apparatus is now at 70° K. The outer vacuum space E_1 is pumped to high vacuum.

1 hr. 20 min. The expansion valve is opened and the hydrogen flow is started. The pressure of hydrogen used is 150 atmospheres. The valve is adjusted to give a flow of 70 litres per minute. The temperature falls rapidly.

1 hr. 24 min. Hydrogen begins to liquefy at the valve. Vessel A is now at 20° K. The hydrogen flow is reduced to 30 litres per minute as with a greater flow the exchanges are inefficient. From time to time liquid air is admitted to the Dewar vessel through the siphon. The level is always kept near the top of the Dewar vessel.

1 hr. 34 min. Regular oscillations on the flow-meter F_1 show that the vessel A is full of liquid. The cooling of the vessels B and C is now started by admitting hydrogen at a pressure of about 3 atmospheres to the vessel B. The hydrogen condenses in passing the vessel A and the liquid falls into B and evaporates again. The cooling is assisted if the outlet tap T_7 of B is partly opened so that there is a flow of about 2 litres per minute through the vessel. When the temperature is about 40° K. the tap T_7 is closed.

1 hr. 43 min. The temperature of B has now reached 20° K. and liquid begins to collect in B, the pressure being kept at 3 atmospheres by adjusting the inlet valve V_{10}. Helium is slowly compressed into the vessel C.

1 hr. 54 min. The vessel B is now full of liquid. This is shown by the fact that if the inlet valve V_{10} is closed completely the pressure remains at 3 atmospheres. Helium is still slowly compressed into C and the liquefaction of hydrogen in A is also continued until the hydrogen-liquefier A is full, and the liquefaction is then stopped. The helium pressure is now 130 atmospheres.

2 hr. 10 min. The pumping off of the condensed hydrogen by the rotary pump P_1 is started.

2 hr. 16 min. The hydrogen in B has reached the triple point 14° K. The pumping of the hydrogen vessel A is started using the pump P_2.

2 hr. 30 min. Hydrogen liquefaction in A is restarted.

2 hr. 40 min. A is full of liquid and the flow is stopped.

3 hr. 5 min. Nearly all the hydrogen in B has now been pumped away and the temperature is about 11° K. The helium pressure is 120 atmospheres. The inner enclosure E_2 is evacuated. The helium is now ready for expansion. The helium inlet valve V_4 is closed and the helium condensation vessel M is connected with the 5-litre flask. The helium outlet valve V_6 is slowly opened so that the expansion of the helium in C is started. During the expansion the taps T_5 and T_7 on the outlet from the vessels A and B are closed.

3 hr. 14 min. The expansion ends. The vessel C now contains liquid helium at 4·2° K. The tap T_5 is opened again.

3 hr. 17 min. 1·5 litres of helium gas have been condensed in M. This is about 1·6 cm³ of liquid helium but is sufficient for cooling the average experimental specimen. It would cool 50 kg. of copper from 4° to 1° K. The pumping of the liquid in M with the high vacuum pump is now begun.

3 hr. 22 min. The vessel M and the specimen K have now reached a steady temperature of 1·3° K. and the low-temperature measurements can begin. The temperature is indicated by the vapour pressure of 1·5 mm. which is read on the mercury manometer.

4 hr. 10 min. The helium liquefier is now empty and begins to warm slowly.

It is convenient and economical to make several expansions in succession. At 5 hr. 40 min. a second expansion and at 8 hr. 10 min. a third expansion could be made. At each expansion the liquid helium in C generally lasts for 1 or 2 hours, depending on the amount of helium which has been condensed in M,* and this is sufficient for most experiments. If it were desired to make experiments for longer times than this it would only be necessary to increase the size of the vessel C so that a greater quantity of liquid could be obtained. The size of the vessels A and B would have to be increased in proportion. It is important that the ratio of the sizes of B and C shall be calculated correctly so that the correct amount of hydrogen for cooling the helium in C may be contained in B.

It is not always necessary to use condensed helium for cooling the specimen K; indeed, for many electrical or magnetic experiments it is sufficient to fix the specimen in thermal contact with the helium vessel C and the temperature can be lowered if necessary to 2° K. by pumping out this vessel. With this arrangement it is not necessary to have even an inner vacuum enclosure.

Sometimes it is more convenient to suspend the specimen in the inner enclosure and to cool it with exchange gas or, of course, the specimen can be enclosed in a copper or glass vessel and cooled in that way. Cooling with exchange gas is not very satisfactory if calorimetric experiments are to be made, as the gas has to be completely pumped away before the experiment is started and this may take a considerable time.

For three expansions the total quantity of liquid air required for the liquefier and the cleaners is about 16 litres, and 6 cubic metres of hydrogen are needed. The greater part of the liquid air (9 litres) is used for the cleaners.

Improvement in the performance of the liquefier could have been obtained by increasing the total length of the apparatus so as to increase the length of the connecting tubes and thus reduce the rate of evaporation of liquid hydrogen and helium.

When once the initial difficulty of handling the apparatus had been overcome it was found possible to make low-temperature experiments regularly and satisfactorily with this liquefier, and calorimetric measurements have recently been made with it on liquid and solid helium. These will be described in a later publication.

* For every cm^3 condensed in M about 4 cm^3 of liquid are evaporated from the liquefier C. The additional 3 cm^3 represents the amount necessary to cool the incoming gas.

§ 7. ACKNOWLEDGMENTS

In conclusion I should like to express my thanks to Prof. Simon, who suggested the construction of this liquefier and has given me very valuable advice and assistance, and to Prof. Lindemann for his interest in the work and for extending to me the facilities of the Clarendon Laboratory. I would like especially to thank Dr Kurti for his advice on the construction of the liquefier and his help with the experiments. The work has been assisted by the receipt of a research grant from the Department of Scientific and Industrial Research.

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ABSORPTION SPECTRA OF THE CHLORIDES AND OXYCHLORIDES OF SULPHUR

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ABSTRACT. The absorption spectra of the vapours of SCl_2, S_2Cl_2, $SOCl_2$ and SO_2Cl_2 have been investigated in the visible and ultraviolet regions, and the continuous absorptions observed are correlated with photodissociation processes.

§ 1. INTRODUCTION

The absorption spectra of these substances have been measured in the liquid state[1,2]. The measurements do not, however, enable one to correlate the energies of dissociation with the regions of selective absorption, for two reasons: (i) it cannot be ascertained whether the maxima are envelopes of a band system or represent true maxima of continuous absorption due to photodissociation; and (ii) the long-wave-length limit of absorption, a knowledge of which is necessary for an understanding of the process of photodissociation, gives too small an energy value, owing, no doubt, to the great number of molecules in higher vibrational levels of the ground state[3]. These difficulties can to a great extent be minimized by studying the absorption of the substances in the state of vapour, and such an investigation has accordingly been undertaken. Preliminary reports of the work have already been published[4].

§ 2. EXPERIMENTAL

The substances were contained in a side bulb attached to the main apparatus consisting of the absorption cell of fused silica and the usual vacuum arrangement with a manometer. The vapour was introduced into the absorption cell after the apparatus had been exhausted, the apparatus being thoroughly washed many times before the final sample of vapour was taken. For work in the ultraviolet, absorption cells of lengths 5, 10 and 20 cm. were used with a hydrogen tube for the source of continuous spectrum and a quartz spectrograph of medium dispersion. Copper arc lines were utilized for standard wave-lengths. For the visible region a glass tube of length 100 cm., to the ends of which were sealed plane glass windows, was used as the absorption cell; the continuous source was a gas-filled 8-volt bulb

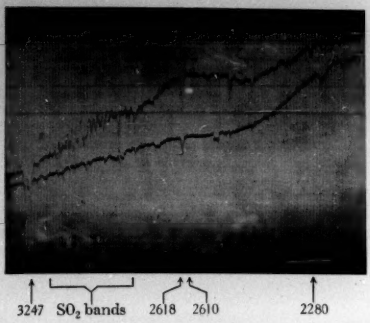


Figure 1. SCl_2 (ultraviolet).

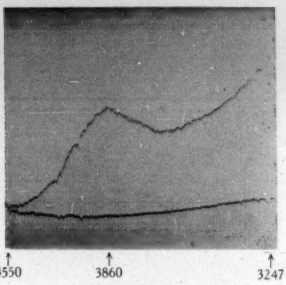


Figure 2. SCl_2 (violet).

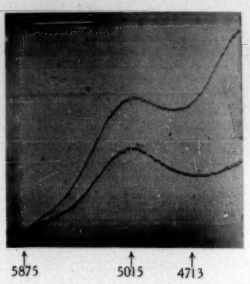


Figure 3. SCl_2 (green).

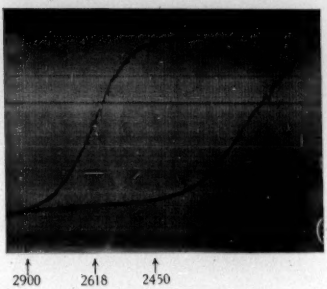


Figure 4. $SOCl_2$.

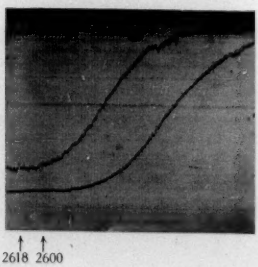


Figure 5. SO_2Cl_2.

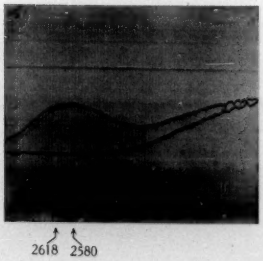


Figure 6. S_2Cl_2.

In each figure the lower curve represents the light source and the upper curve indicates the absorption.

To face page 29

having a straight filament which during the exposure-time was run on a constant voltage of 10. The resolving instrument was a Hilger constant-deviation glass spectrograph. The necessary standard lines were given by the helium-plus-mercury discharge tube. The plates were measured on the recording photometer; the long-wave-length limits and the positions of the maxima of absorption were determined from the microphotometer plates. All the substances have a great tendency to exhibit SO_2 bands in absorption, but this tendency was minimized by careful and repeated washing of the apparatus with the vapour, distillation of the liquids in high vacuum, and the use of glass needle valves after Bodenstein[5]. Some of the plates, especially those for SCl_2, showed bands which did not completely agree in appearance with the well-known absorption bands of SO_2. Actual measurement and analysis, however, have convinced us that all these bands, some of which have not previously been classified, are to be attributed to SO_2; and the results of the analysis will be recorded in a separate communication.

§ 3. RESULTS AND DISCUSSION

The absorption by sulphur dichloride is continuous and exhibits three maxima, as will be seen in the microphotometer plates, figures 1 to 3, and in the diagram, figure 7. Starting from the short-wave side, we find the first absorption region of about 90 A. from λ 2350 to λ 2260 with a maximum at λ 2280. The second region occupies about 320 A. from λ 2770 to λ 2450, with a maximum at λ 2610. The beginning of the third absorption appears to be at λ 4550 on a Wellington anti-screen plate in the quartz spectrograph, but at λ 5825, with a definite inflection at λ 5165, on a panchromatic plate in the glass spectrograph; this absorption has a maximum at λ 3860 and ends at λ 3700. It is found[6] that Cl_2O shows two corresponding maxima, one due to the photodissociation into $ClO + Cl$, the other into $(ClO)^* + Cl$, the energy-difference between the two being 2800 cm.$^{-1}$ The energy of excitation of SCl should be slightly less than this value. The difference between $\lambda\lambda$ 5165 and 5825, which is 2193 cm.$^{-1}$, may therefore roughly represent the difference between the two long-wave limits of the photodissociation processes corresponding to those of Cl_2O mentioned above. Since, however, real maxima could not be found, and the absorption curves of many substances show a lengthening on the long-wave side, due evidently to losses by reflection very similar in appearance to the curve in figure 7, we prefer to take λ 5165 as the real long-wave limit of the first process of photodissociation of the SCl_2 molecules ($SCl_2 \rightarrow SCl + Cl$). Even if λ 5825, and not λ 5165, represents the energy of the photodissociation, the difference, 2193 cm.$^{-1}$, is well within errors of computation.

Thionyl chloride, $SOCl_2$, figure 4, shows one region of absorption of width 500 A., from λ 2900 to λ 2400, with a maximum at λ 2450. Sulphuryl chloride, SO_2Cl_2, figure 5, gives one continuous absorption starting from 2600 A., with no maximum within the limit of the quartz region. Sulphur monochloride, S_2Cl_2, figure 6, has an absorption region of 380 A. from λ 2770 to λ 2390 with a maximum at λ 2580. The data are collected in table 1.

All these regions of continuous absorption are due to transitions from the normal states of the molecules to various excited repulsive states. The breadth of the absorption region is a measure of the steepness of the repulsive curve. This steepness increases from SCl_2 to SO_2Cl_2 in the order given in the table. With the exception of SO_2Cl_2, where the region of absorption appears to be very extensive, the repulsive curves are relatively flat and the agreement between the computed

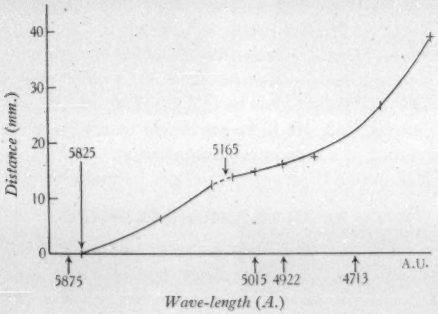


Figure 7. Showing the distance between two curves of figure 3, for SCl_2.

energy of dissociation and the long-wave limit clearly indicates that the photolytic processes involved produce unexcited dissociation products, with the exception of the absorption at λ 2350 in the case of SCl_2. Similar agreement obtains also for SO_2Cl_2, which shows that although the repulsive curve is relatively steep the products of dissociation are unexcited. The observed maxima represent the most probable values of the kinetic energy of the products of dissociation, indicated by the relative positions of the curves in the Franck-Condon diagram.

Table 1. Wave-lengths (A.) of the beginning *a*, maxima *b*, and ends *c* of the absorption regions. Figures in parentheses are the corresponding numbers of kcal./mol.

	I		II			III			IV		
	a	*b*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
SCl_2	5825 (48·5)	5165 (55·4)	4550 (62·4)	3860	3700	2770 (104)	2610	2450	2350 (122·4)	2280	2260
S_2Cl_2						2770 (104)	2580	2390			
$SOCl_2$						2900 (97)	2450	2400			
SO_2Cl_2									2600 continuous → (108·6)		

The thermochemical values given in table 2 represent the heat of formation from the constituent atoms in the gaseous state and are obtained in the usual way from data given by the Landolt-Börnstein Tables. For the energy of dissociation of S_2 we do not use the value 102·6 kcal./mol. determined[7] by predissociation in the band spectrum of S_2,* but prefer to calculate it from the point of convergence of the absorption bands ($B\,^3\Sigma \leftarrow X\,^3\Sigma$) which has been directly observed[8] at 40,000 ± 1000 cm.$^{-1}$ Deducting from this the energy, 9240 cm.$^{-1}$, of excitation of ^1D state of sulphur[9] we obtain 30,760 ± 1000 cm.$^{-1}$ or about 90 kcal./mol. as the energy of dissociation of S_2 into two unexcited S atoms.†

Table 2

$S+2O$	$=SO_2$	$+248$ kcal./mol.
$S+2Cl$	$=SCl_2$	$+123$,,
$S+O+2Cl$	$=SOCl_2$	$+215$,,
$2S+2Cl$	$=S_2Cl_2$	$+185$,,
$S+2O+2Cl$	$=SO_2Cl_2$	$+317$,,
$S+3O$	$=SO_3$	$+330$,,

The value for SCl_2 appears to be slightly less reliable.

The long-wave-length limit of SO_2Cl_2 gives 108·6 kcal./mol. and the difference between the heats of formation of SO_2Cl_2 and $SOCl_2$ is 102 kcal./mol. Since it is never possible to follow the long-wave-length limit right up to the point where the products of dissociation have zero kinetic energy, the agreement is very good. So the absorption at λ 2600 represents the dissociation of SO_2Cl_2 into unexcited $SOCl_2+O$. The maximum of absorption is evidently below the quartz region and is in a different position from that of the other substances.

All the other substances exhibit a common absorption in the region between λ 2400 and λ 2900. It is not possible to explain away this common absorption as due to a common impurity; this is clearly shown by the absorption curves for the liquid state, where the maximum for each substance represents a higher value of the absorption coefficient than could be yielded by an impurity. Again, it is unreasonable to attribute the common absorption to different processes of photodissociation in different molecules. It is true that the positions of the maxima and their long-wave limits are not exactly identical, but the differences are clearly due to the fact that, as we now know, the law of additivity in the case of bond energies holds good only in zeroth approximation[10], and already the differences in the repulsive forces in the different molecules spoil the exact operation of this law. So this absorption has to be taken as characteristic for each molecule. Since only the SCl linkage is common to all these molecules, it is this that is involved in this absorption. Further, for the following reasons, this continuous absorption must mean the splitting off of the Cl atoms. The long-wave limits of the maxima give us directly values of about 104 kcal./mol. for S_2Cl_2 and 97 kcal./mol. for

* Linear extrapolation of the vibrational levels of the S_2 molecule will give too high a value for the dissociation energy on account of the existence of perturbations in a number of these levels. Predissociation data also naturally yield values that are too high.

† This point is discussed in greater detail in a forthcoming paper by one of us.

$SOCl_2$. If only one Cl were split off, the removal of the second Cl would further involve nearly the same energy-change, if not a slightly greater one on account of the repulsion of the two Cl atoms. On this basis, therefore, about 200 kcal./mol. would be used up for the two SCl bonds; and since the atomic heats of formation for $SOCl_2$ and S_2Cl_2 are 215 and 185 kcal./mol., only about 15 kcal./mol. would be left over for the S=O bond and none at all for the S=S bond. This is obviously impossible. If, however, we deduct 97 kcal./mol. from the energy of formation of $SOCl_2$, and 104 kcal./mol. from that of S_2Cl_2, there remain 118 kcal./mol. for the double bond in SO and 88 kcal./mol. for the double bond in SS. From band-spectrum data we obtain, for the SO bond, 117·6 kcal./mol. for the ground state of SO[11], and 90 kcal./mol. for the SS bond as was shown above. The agreement is very good. We have further evidence in favour of this view. This difference of 102 kcal./mol. between the energies of formation of SO_2Cl_2 and $SOCl_2$ indicates that the energy of this double bond in the diatomic molecule still prevails as true bond energy in the polyatomic molecule, modified rather than changed by the difference in the forces of repulsion. This is so because the electronic configuration of a diatomic molecule of the type SO, S_2, etc. need not suffer any change when the molecule becomes polyatomic, the diatomic molecule already possessing two free valencies in the $^3\Sigma$ ground state. Again, half the atomic heat of formation of SO_2, namely 124 kcal./mol., is about equal to the above value of 118 kcal./mol. for the double bond in SO. But the difference of 88 kcal./mol. between the energies of formation of SO_2 and SO_3 gives a considerably smaller value for the third bond in SO_3. In any case it is clear that the common absorption region certainly corresponds to the splitting off of both the chlorine atoms in these molecules.

This view is further corroborated by the absorption spectrum of SCl_2. In this case the absorption on the long-wave side corresponds to the splitting off of one Cl atom, and the second one, therefore, to the splitting off of the second Cl in addition to the first. As there are only two bonds, no other explanation is possible if the common absorption is to be properly correlated. Indeed the value 55·4 kcal./mol., which is obtained from the long-wave limit λ 5165, is near to half the total energy of formation of SCl_2, namely 61·5 kcal./mol. The value 123 kcal./mol. is, as has already been stated, a rough one, for here the original measurements from which it is derived are obtained by indirect experiments which in reality give the heat formation of SCl_2 in solution with S_2Cl_2. The long-wave limit at λ 2770, i.e. about 104 kcal./mol., represents the splitting off of the second Cl atom also.

The absorption beginning at λ 2350 has to be correlated with the dissociation into at least one excited product. The repulsive curve in this case is very flat, because the width of the region is small and, therefore, indicates that it does not run down to the ground level of the separated system of unexcited products. The energy-difference of the two long-wave limits, λ 2350 and λ 2770, is 6450 cm^{-1}. We correlate this region of absorption to the process of dissociation of SCl_2 into $2Cl + S\,(^1D)$. The energy of excitation of this ^1D state is about 9240 cm^{-1}. The agreement is not satisfactory, but better agreement is rather difficult to expect in view of the facts that the two repulsive curves obviously do not run parallel, that

the long-wave limit is never well defined, and that the difference in energy which is being sought is in itself small.

§ 4. OPTICAL VALUES OF BOND ENERGIES

The values of the bond energies derived from optical measurements here and elsewhere are given in table 3.

Table 3

Number of bonds	Designation of bonds	Derivation of bonds	Bond energy kcal./mol.
Two	S—Cl	S_2Cl_2	104
Two	S—Cl	$SOCl_2$	97
Two	S—Cl	SCl_2	104
One	S—Cl	SCl	55·4
One	S=O	$SOCl_2$	118
One	S=O	SO*	117·6
One	S=O	SO_2Cl_2	108·6
One	S=S	S_2Cl_2	88
One	S=S	S_2*	90

* Taken from band-spectrum data.

On account of the forces of repulsion, the energy of the SCl bond should indeed be lower in $SOCl_2$ than in S_2Cl_2, and lower for the second than for the first bond in SCl_2; and the energy of the SO bond should be lower in SO_2Cl_2 than in $SOCl_2$.

§ 5. CONCLUSIONS

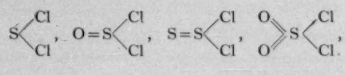
The following observations upon the work which has been described will perhaps not be out of place.

(i) The first process of dissociation of SO_2Cl_2 concerns the splitting off of an O and not a Cl atom in spite of the fact that the double bond of O represents a higher energy than that of the single bond of Cl. This is probably so because the oxidation of $SOCl_2$ into SO_2Cl_2 involves the activation of the two original *s* electrons of S, which still form a repulsive group in the tetravalent sulphur. Therefore this is the first loss which occurs to SO_2Cl_2. The low value of the third SO bond in SO_3 might also be connected with this phenomenon. As in CO_2[12], the ground state of the diamagnetic SO_3 molecule does not originate from O (^3P) plus the ground state of the diamagnetic SO_2, but from an excited term of SO_2.

(ii) The energies per bond remain rather constant in all these molecules.

(iii) In SCl_2 we observe two different processes of photodissociation whereby the first link and then the second link undergoes fission, as in Cl_2O. In $SOCl_2$ and S_2Cl_2, in which all the four *p* electrons of S share in the linkage, the first photolytic process breaks up both SCl links. A process in which only one Cl atom is split off does not occur, or rather occurs with such low probability that the corresponding absorption cannot be found; otherwise these substances would be strongly coloured like SCl_2.

(iv) We have assumed in this paper that the structure of the molecules corresponds to the classical formulae such as



each bond representing a pair of electrons, one belonging to each atom. Other formulae implying semipolar double bonds and singlet linkages have been based on the measurements of the parachors of these substances, but recently it has been shown[13] that molecular parachors do not provide diagnostic information with regard to the nature of the linkage in such cases. On the other hand, the Raman effect establishes[14] the validity of the above chemical formulae, and the fact that the bond energies remain nearly unaltered in these molecules, as has been shown above, as well as in related ones like SO, S_2, SO_2, etc., is entirely consonant with this view.

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THE INTEGRATION OF THE GLARE EFFECTS FROM A NUMBER OF GLARE SOURCES

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ABSTRACT. The effect of a number of glare sources on indirect vision, 5° above the fovea, is shown to be equal to the sum of their separate effects, the criterion of equality being that the equivalent background brightness of all the sources measured together is the same as the sum of the equivalent background brightnesses measured separately.

§ 1. INTRODUCTION

It has been shown by Holladay and by Stiles[1] that the effect of a glare source in the field of view of an observer upon the brightness difference threshold is equivalent to that of a uniform background of a certain brightness given by

$$\beta = \frac{kE}{\theta^n} + B \qquad \text{.....(1),}$$

where β is the equivalent background brightness, E is the illumination at the eye of the observer due to the glare source, θ is the angle subtended at the eye between glare source and threshold test area, B is the actual background brightness and k and n are constants. k and n have approximately the values 10 and 2 respectively. Holladay further showed that, if a number of glare sources were visible in the field of view, the total effect was equivalent to a background brightness given by

β, E θ B k, n

$$\beta = k\left(\frac{E_1}{\theta_1^n} + \frac{E_2}{\theta_2^n} + \ldots + \frac{E_p}{\theta_p^n}\right) \qquad \text{.....(2),}$$

E_p, θ_p

where suffixes 1, 2 ... p refer to the several glare sources. Holladay's work on these points was done with a test spot of maximum diameter 0·47° centred at the fovea of the observer's eye. The type of vision concerned was therefore purely foveal. A larger test spot, even though centred at the fovea, may give results showing a mixture of foveal and parafoveal types of vision.

In the extension of the equivalent background brightness formula to the general case, in which the test spot may fall on retinal areas other than the fovea, one of the steps is to show that the summation expressed in equation (2) is valid for such areas. In the present communication this is demonstrated for a small test area of the retina 5° above the fovea. Distance and direction relate to the external field of view.

§ 2. EXPERIMENTAL CONDITIONS

The following arrays of glare sources were used. (*a*) A circle of twelve equally spaced glare sources centred at the test spot and of radius 3·05°. The glare sources were small 4-volt 2-watt lamps, the current through each being adjusted so that their candle powers were very nearly equal. (*b*) A circle of glare sources similar to

(*a*) but of diameter 14·6°. (*c*) Twelve glare sources arranged in a spiral of one turn, the distances of the sources from the test spot increasing from 1·03 to 19·7° in a geometric series. Each glare source was adjusted in intensity so that it gave approximately the same equivalent background brightness at the test spot. That is, the intensity of each glare source was inversely proportional to the square of its angular distance from the test spot.

In all cases the background brightness under glare conditions was zero.

§ 3. EXPERIMENTAL PROCEDURE

With each of these arrays of glare sources the equivalent background brightness of the sources was measured separately, and then the equivalent background of the whole array was determined. The latter value should equal the sum of the individual equivalent backgrounds if the summation law holds.

The determination of an equivalent background involves a measurement of threshold under the glare conditions and a measurement of the background brightness giving the same threshold. The latter is most easily obtained from a curve of threshold against background brightness. To supply these data, readings were taken according to the following plan: (*a*) one threshold reading for each glare source taken separately in a random order; (*b*) six threshold readings for the whole array of glare sources; (*c*) six threshold readings for each of a series of four or five background brightnesses covering the necessary range; (*d*) a repetition of (*b*).

All threshold readings for this work were taken with the brightness difference threshold meter described by Crawford and Stiles[2]. The test spot in this instrument is exposed for a short flash of duration 1/400 second; its diameter is approximately 0·05°.

§ 4. RESULTS

The table shows the results obtained.

Table 1

Glare-source array	Observer	Sum of equivalent backgrounds for each lamp measured separately (candle/ft^2)	Equivalent background for all lamps measured together (candle/ft^2)	Difference per cent
(*a*)	B. H. C.	·103	·100	+ 3
(*a*)	F. W. C.	·137	·100	+37
(*b*)	B. H. C.	·036	·047	−23
(*b*)	F. W. C.	·046	·039	+18
(*c*)	B. H. C.	·027	·027	0
(*c*)	F. W. C.	·019	·035	−17
(*c*)	F. W. C. (second series)	·026	·028	− 7
(*c*)	C. D.	·030	·027	+11
			Mean difference	+ 3
			Mean error	± 15

These results may be taken to demonstrate the approximate validity of the additive law. Each pair of figures given is the result of two to three complete runs taken within a few days of each other. It would appear that an observer may sometimes show a consistent difference between equivalent background brightnesses determined separately and collectively, but on the average of all the results the difference is negligible.

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612.843.35

THE DISCRIMINATION OF THE SATURATION OF COLOURS

By F. L. WARBURTON, A.R.C.S., D.I.C., M.Sc., A.Inst.P.

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ABSTRACT. Recent data on the sensitivity to saturation-differences have been correlated with the complementary colour-mixture data for the same observer. The experimental results are discussed on the basis of the three-component theory of Young and Helmholtz, and an attempt has been made to explain them by applying Weber's law to the component colours of the theory.

§ 1. INTRODUCTION

In a paper presented at the Physical Society's discussion on vision[1] jointly by Dr L. C. Martin, Mr W. J. Morgan and the author, a preliminary account was given of some experimental work on the sensitivity of the eye to differences in the saturation of colours. The work has since been completed by the same workers and a full experimental account has been published by the Medical Research Council in their Special Report Series[2]. In neither of these papers has more than a brief account been given of the theoretical aspects of the work. In the present paper the results are discussed on the basis of the Young-Helmholtz theory.

In investigating the sensitivity of the eye to saturation-differences two main methods of approach were adopted. In the first the total number of perceptible steps between each of a number of pure spectral colours and white was determined, either by adding the colour to white step by step until the mixture contained only spectral light, or *vice versa*. In this way the colorimetric purity of each step can be

L_C obtained as follows. If L_C is the luminosity of the colour,

$$L_C = L_S + L_W,$$

L_S, L_W where L_S is the luminosity of the spectral component and L_W that of the white.

p Then the colorimetric purity $p = L_S/L_C$. This method gives a fairly accurate measure of the total number of steps between each spectral colour and white, and a somewhat less accurate measure of the variation in the size of the purity-discrimination limen Δp with colorimetric purity. The relation between the total number of steps and the wave-length is shown in figure 1.

In the second method the colorimetric purity of the colour just discriminable from white for each hue has been determined with a considerable degree of accuracy by making a large number of successive determinations. The results have been given

L_C' by plotting L_C'/L_S for this colour against the wave-length λ, figures 2 and 3.

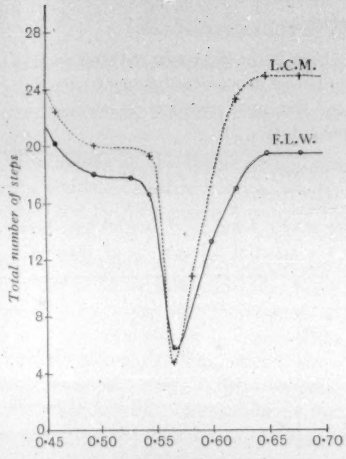

Figure 1.*

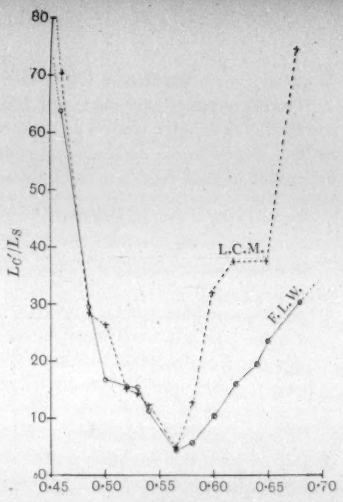

Figure 2.* Variation of L_C'/L_S with wave-length. Eyes dark-adapted.

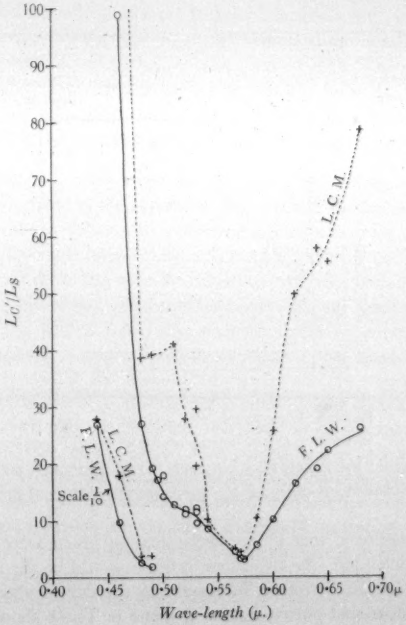

Figure 3. Variation of L_C'/L_S with wave-length. Eyes light-adapted.

* From a paper in the *Discussion on Vision*, pp. 98, 99.

The observations were made with the eye both in the light-adapted state and the so-called dark-adapted state. The most complete set of results obtained by the first method related to the dark-adapted state, and the most complete set obtained by the second method related to the light-adapted state.

§ 2. COMPARISON OF THE RESULTS OBTAINED BY THE TWO METHODS

Both the curves relating the number of steps with λ and L_C'/L_S with λ have been taken as showing the relative saturation of the spectral colours. It is, therefore,

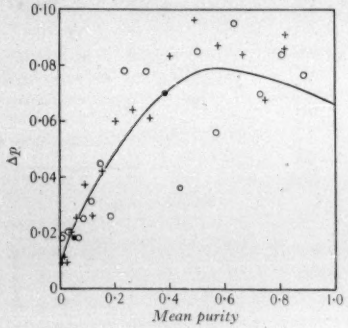

Figure 4. Wave-length, 0·46 μ.; observer, F. L. W.

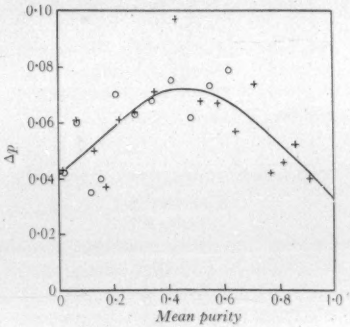

Figure 5. Wave-length, 0·496 μ.; observer, F. L. W.

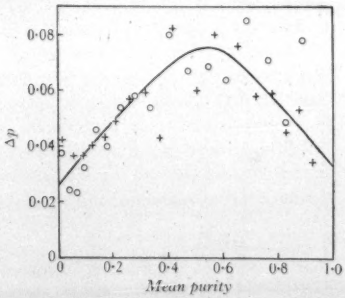

Figure 6. Wave-length, 0·65 μ.; observer, F. L. W.

Figures 4–6. Variation in size of limen with purity for different wave-lengths.

important to consider the differences between them. The most striking difference is the saturation for blue as given by L_C'/L_S as compared with that given by the number of steps.

It may be mentioned that if the discrimination limen were the same for all purities for any given hue, the two types of curve would be the same. The reason for the difference must, therefore, be sought in the curves showing the relation between size of limen and purity, figures 4, 5 and 6. These show for blue a great

increase in the size of the limen with increasing purity, whether the results are obtained by desaturating the spectral colour or by adding blue to white. For the other colours there is at first a slight increase followed by a decrease to the original value.

The reason for this difference is obscure; it may possibly be due to eye-movements and lack of foveal fixation, which is very difficult for the blue as has been pointed out by Abney and Watson[3]. The fact that the rise is more marked for L. C. M., who has a very small pigmented area, would favour this view. The total number of steps for the extreme blue cannot, however, be very much in error, and there cannot be the same difference between the ordinates for 0·46μ. and 0·50μ. as in the L_C'/L_S curves, for otherwise the difference in the total number of steps between white and 0·46μ. and between white and 0·50μ., namely more than 40, would be greater than the total number of steps between these colours on the spectrum locus, namely about 15. If this were so, it would be possible to get fewer steps between white and the extreme blue by first proceeding along the spectrum locus to the blue green and then desaturating, and this is very unlikely to be the case. These considerations thus point to a greatly decreased sensitivity in the neighbourhood of the saturated blue. This view would appear to be supported by some recent work of Tyndall[4] on the sensitivity to difference in hue at different saturations. He finds that for hues corresponding to wave-lengths less than 0·49μ. the sensitivity passes through a maximum with decreasing purity instead of continually decreasing. The effect becomes more marked with decreasing wave-length. The effect may be due to extra foveal vision always being used when these colours are viewed.

§ 3. CORRELATION WITH COMPLEMENTARY COLOUR-MIXTURE DATA

Helmholtz and others have suggested that the ratio of the luminosities in which two colours mix to give white is the inverse of their relative saturations. The most complete set of data on the relative luminosities of such colours when mixed to produce white is that due to Sinden[5]. By assuming that the saturation is practically constant in the yellow, he has used his results to give what he calls the relative saturation of the spectral colours. The resultant curve is very similar to that obtained by plotting L_C'/L_S against λ, and this suggests that the relative luminosities of spectral complementaries is proportional to the relative purities of those colours of the same hues which are just distinguishable from white. The only direct way of obtaining a precise comparison of the complementary-colour data with the discrimination data is to use the former to obtain the values of L_C'/L_C for the red hues from those for the blue hues, or *vice versa*. This comparison is strictly valid only if the two sets of data refer to the same neutral standard and the same observer. No such data are available. In the absence of direct data similar to Sinden's (that is to say, data relating to what has been called the complementation valency), the information can be obtained indirectly from the trichromatic coefficients of the spectral colours and white, provided that the relative luminosities of the unitary stimuli also are known.

The trichromatic coefficients of the spectral colours and white have been obtained for one observer (F. L. W.) and also the luminosities of the unitary stimuli. The method used for both these sets of observations was identical with that

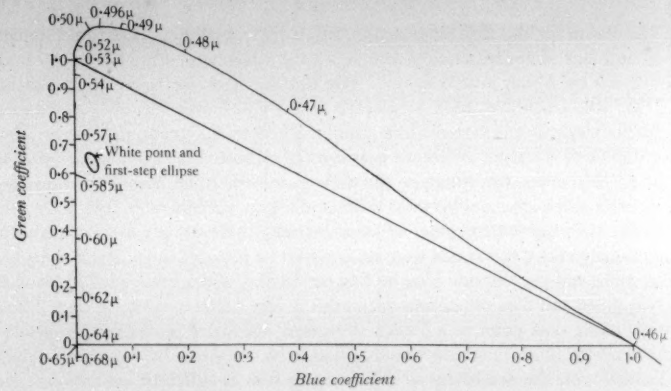

Figure 7 *a*. Colour triangle showing locus of colours just discriminable from white.

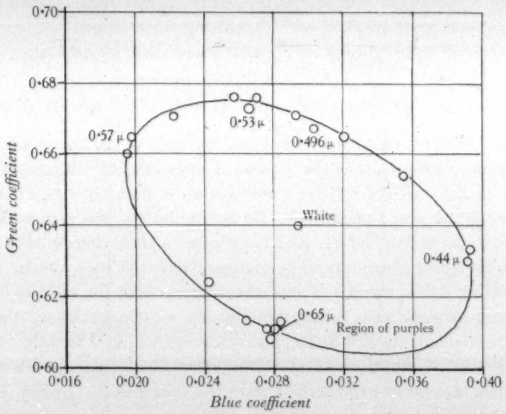

Figure 7 *b*. Locus of colours just discriminable from white on an enlarged scale.

described by W. D. Wright[6]. For the purpose of determining the luminosities, a large number of flicker matches and determinations of the red and blue correction factors were made, a high degree of precision in the results being thus ensured.

By means of the above data, the units in which the unitary stimuli R', G' and B' are measured can be transformed to the same photometric scale. One trichromatic

unit will then have the same photometric value for all colours. By the use of these coefficients for the spectral colours and white, the coefficients for the colours just discriminable from white can be directly obtained in photometric units, and the locus of these colours in the equal-brightness triangle can be plotted. This is found to be an ellipse with white at the centre.

Alternatively the coefficients so found can be transformed to any other units before the locus is plotted. When this is done the locus remains an ellipse, but the white point is no longer at the centre.

With reference to the equal-brightness triangle, if m is the distance of a spectral colour from white and p the purity of the colour of this hue just discriminable from white, the distance of this latter colour from white is pm. If n and p' are the corresponding quantities for the complementary colour, we have—since the colours just discriminable from white lay on an ellipse—

m
p
n, p'

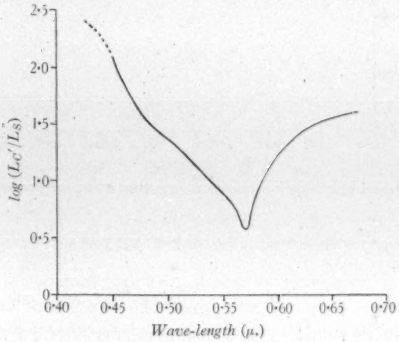

Figure 8. Variation of L_C'/L_S with wave-length; mean logarithmic curve.

$$pm = p'n,$$
$$m/n = p'/p.$$

But m/n is the ratio in which these colours mix to produce white. There is thus a precise correspondence between the complementary-colour data and the data concerning colours just discriminable from white.

The curves showing the relation between L_C'/L_S and λ for the observers L. C. M. and F. L. W. are so similar to those found by Priest and Brickwedde[7] that after reduction of their results by a constant factor, on account of their different field-size, a mean curve has been drawn for all four observers, as being a fairly near approach to the result for a mean eye. These results have been used to obtain a number of points on the locus in the standard triangle of the colours just discriminable from white by a mean observer. The triangle used was that of the C.I.E. committee on colorimetry with the appropriate luminosity factors. The result is shown in figure 9. The extreme eccentricity of the white is due mainly to the luminosity factors not being representative of the four observers used, but partly

to the fact that the white used by Priest and Brickwedde differs slightly from that of the C.I.E. The distance of many of the points from the curve is due to difficulty in reading the correct value of L_C'/L_S from Priest's curves, especially in the yellow, where it is changing rapidly with wave-length.

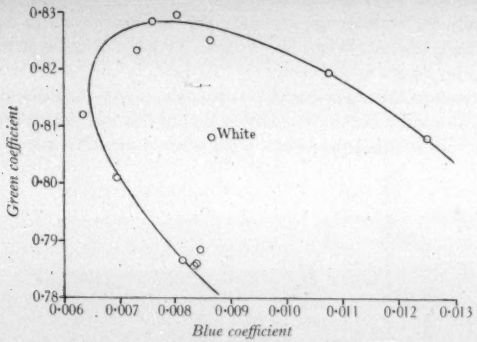

Figure 9. Locus of colours just discriminable from white for a mean observer.

§ 4. INTERPRETATION OF THE RESULTS

Previous attempts to interpret saturation-discrimination by the three-component theory have proceeded along two main lines. The commonest has been the use of the theory to obtain the absolute purity of a colour, together with the postulate that all colours just discriminable from white have the same absolute purity. This has been carried out in the following manner. The general form of the theory states that the trichromatic coefficients of all colours can be transformed to a set of fundamental unitary stimuli R, G and B, for which the coefficients r, g and b are always positive. In this case r, g and b are proportional to the values of the stimuli exerted by the radiation producing the colour upon three independent physiological mechanisms, thus all stimuli which have the same value of r excite the same response in the red receptor.

R, G, B
r, g, b

If we draw a colour triangle using real unitary stimuli R', G' and B', these three fundamental stimuli will have co-ordinates $(\rho_1, \gamma_1, \beta_1)$, $(\rho_2, \gamma_2, \beta_2)$ and $(\rho_3, \gamma_3, \beta_3)$. If these points are then joined to form a new triangle, all physiologically possible colours must lie within this triangle, and therefore the colours lying along the boundary are the purest obtainable; they may, therefore, be considered as having unit absolute purity. If the point $(\rho_W, \gamma_W, \beta_W)$ representing white be given zero purity, then since any other colour can be considered to be the result of the mixture of this stimulus and that corresponding to some colour on the boundary, the absolute purity of such a colour will be given by

R', G', B'
ρ, γ, β

$$P = L_D/L_C,$$

where L_D is the luminosity of the boundary stimulus associated with a quantity of the colour having a luminosity L_C. L_D

In the case where photometric units have been used for R', G' and B', Newton's law of colour-mixture gives, figure 10,

$$L_D/L_C = WC/DW.$$

The locus of colours of equal absolute purity is thus a triangle with its sides parallel to those of the triangle RGB and with its apices on the lines WR, WG and WB. It is thus a triangle in any colour triangle. It has, however, been shown above that the locus of colours just discriminable from white is an ellipse. There is thus no connection between absolute purity as defined above and the minimum perceptible

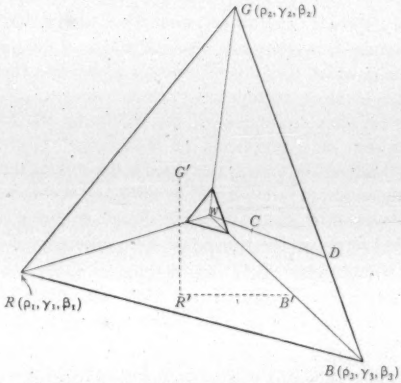

Figure 10. Colours of equal absolute purity.

colorimetric purity, even in the case of complementary colours, which is considered analytically below.

It is frequently assumed that when R, G and B are measured in photometric units the coefficients r_W, g_W and b_W of white are all equal. In this case the absolute purity P_X of a colour X for which r is less than g or b is given by P_X

$$P_X = \frac{b_X + g_X - 2r_X}{r_X + g_X + b_X} \qquad \text{.....(4·1).}$$

The complementary colour Y may then have b less than r or g,

$$P_Y = \frac{r_Y + g_Y - 2b_Y}{r_Y + g_Y + b_Y} \qquad \text{.....(4·2).} \qquad P_Y$$

If the coefficients are those of unit equations

$$\frac{P_X}{P_Y} = \frac{b_X + g_X - 2r_X}{r_Y + g_Y - 2b_Y} \qquad \text{.....(4·3).}$$

On the other hand, if the complementary has g less than r or b,

$$\frac{P_X}{P_Y}=\frac{b_X+g_X-2r_X}{r_Y+b_Y-2g_Y}.$$

If these colours are mixed in the proportion of m units of X and n units of Y they produce white:

$$\begin{gathered}mr_X+nr_Y=mg_X+ng_Y=mb_X+nb_Y,\\ m\,(r_X+g_X)+n\,(r_Y+g_Y)=2\,(mb_X+nb_Y),\\ m\,(r_X+g_X-2b_X)=-n\,(r_Y+g_Y-2b_Y),\\ \frac{n}{m}=-\frac{r_X+g_X-2b_X}{r_Y+g_Y-2b_Y}=-\frac{r_X+b_X-2g_X}{r_Y+b_Y-2g_Y}=-\frac{g_X+b_X-2r_X}{g_Y+b_Y-2r_Y} \qquad \text{.....(4·4).}\end{gathered}$$

On such a theory, there is therefore no connection, such as has been assumed by Hecht and other writers[8], between the absolute purity of complementary colours and the proportions in which they mix to produce white, and therefore there is no connection with the just-discriminable colorimetric purities.

The other method of interpretation of the results on the basis of the three-components theory rests on a suggestion of Helmholtz[9] that colour-differences arise from intensity-differences among the three independent sensations. Colour-discrimination is, therefore, to be explained by applying Weber's law in some form to the fundamental stimuli R, G and B of the theory. Weber's law states that for
ΔL colours of moderate brightness the just-perceptible difference of intensity ΔL between two colours is given by

$$\frac{\Delta L}{\overline{L}}=\text{constant} \qquad \text{.....(5·0),}$$

$\overline{L}$ where $\overline{L}$ is the mean brightness of the two colours. Applying this to the general case where a colour may change in quality as well as in intensity, we get

$$f\left(\frac{\Delta r}{\overline{r}},\ \frac{\Delta g}{\overline{g}},\ \frac{\Delta b}{\overline{b}}\right)=\text{constant} \qquad \text{.....(5·1).}$$

Since there is to be a perceptible change when there is no intensity-difference, the terms in Δr, Δg and Δb must be of the second order.

The simplest function is

$$\left(\frac{\Delta r}{\overline{r}}\right)^2+\left(\frac{\Delta g}{\overline{g}}\right)^2+\left(\frac{\Delta b}{\overline{b}}\right)^2=\text{constant} \qquad \text{.....(5·11).}$$

If the function is to account for brightness-discrimination as well as colour-discrimination, it should include the simple form of Weber's law as a special case. This is, however, not the case with the above simple form, as the value of $\Delta L/\overline{L}$ is different for different colours[10]. Schrödinger[11] has, therefore, proposed the formula

$$\frac{1}{a_1\overline{r}+a_2\overline{g}+a_3\overline{b}}\left\{\frac{(\Delta r)^2}{a_1\overline{r}}+\frac{(\Delta g)^2}{a_2\overline{g}}+\frac{(\Delta b)^2}{a_3\overline{b}}\right\}=\text{constant} \qquad \text{.....(5·12),}$$

which does include Weber's law as a special case. For all changes from a particular colour,

$$x(\Delta r)^2+y(\Delta g)^2+z(\Delta b)^2=\text{constant} \qquad \text{.....(5·2)},$$

whatever units are used for R, G and B.

Various other formulae have been suggested[12], but they all reduce to the same simple form when r, g and b are all large compared with Δr, Δg and Δb.

In considering changes in colour alone this equation must be combined with the condition that there is to be no change in brightness. Since the luminosity of any colour is given by

$$L_C=L_R r+L_G g+L_B b,$$

this condition is

$$O=\Delta L_C=L_R\Delta r+L_G\Delta g+L_B\Delta b,$$

$$\therefore\ \Delta b=-\frac{L_R}{L_B}\Delta r-\frac{L_G}{L_B}\Delta g \qquad \text{.....(5·3)}.$$

If we consider changes in all directions from white, these equations become

$$x(r-r_W)^2+y(g-g_W)^2+z(b-b_W)^2=0 \qquad \text{.....(5·21)},$$

$$(b-b_W)=-\frac{1}{L_B}\{L_R(r-r_W)+L_G(g-g_W)\} \qquad \text{.....(5·31)}.$$

Considered geometrically, equation (5·21) gives the locus in Lambert's pyramid of all colours just discriminable from white, and equation (5·31) is the equation of the equal-brightness plane through white. Their intercept gives the locus in the equal-brightness plane of colours which can just be discriminated from white of the same luminosity, and is an ellipse with white at the centre. When R, G and B are measured in photometric units, this plane is also the unit plane and is the plane of the unit triangle. Hence the locus in the equal-brightness triangle of colours just discriminable from white is an ellipse with white at the centre. In other cases this plane is not the unit plane; the locus in the unit plane is then the projection from the origin, on to that plane, of the locus in the equal-brightness plane. This also will be an ellipse, but the white point will no longer be at the centre since in the projection of a conic from a point not at infinity the centre does not project to the new centre.

The theory is thus consistent with the facts of colour-sensitivity in the neighbourhood of white. A satisfactory explanation of the variation in sensitivity with purity has not proved to be possible.

§ 5. ACKNOWLEDGMENT

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FINE STRUCTURE IN THE (^{2}D) SERIES LIMIT TERMS OF THE I^+ SPECTRUM

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ABSTRACT. The eleven lines of the I^+ spectrum which were previously analysed for fine structure belong to the (^{4}S) system. The analysis is now extended to the (^{2}D) system, fourteen lines having been analysed and fine-structure interval factors found for twelve terms. This brings the known number of interval factors up to twenty-three. Large interval factors are found associated with the $5d$ electron terms of both the systems. This is correlated with observations in the Sn II fine structures, and it is shown that the large $5d$ interval factors are due to perturbation by terms with large fine structure. Two types of perturbation in the fine structures are observed.

§ 1. INTRODUCTION

The author has already published measurements of the fine structures of the visible lines in the first spark spectrum of iodine[1]. At the time of writing only a partial analysis of the gross multiplet structure was available, Murakawa[2] being responsible for this classification. Eleven out of the forty-two lines whose structures were recorded, were classified by Murakawa. From these lines it was proved that the nuclear spin of iodine is 5/2, this value being later confirmed by an analysis of the fine structures in the arc spectrum of iodine[3].

Recently a very thorough multiplet classification for I^+ has been made by Lacroute[4], who by employing the Zeeman effect classified over two hundred lines and identified fifty-four terms. The Zeeman-effect observations agree with the 5/2 value for the nuclear spin. Lacroute showed that the analysis given by Murakawa is correct, and further that all the lines classified by Murakawa and analysed for fine structure[2] are lines in which both the terms go to the (^{4}S) series limit. Amongst the forty-two previously recorded fine structures, fourteen lines have both terms belonging to the (^{2}D) series limit, according to Lacroute. No intercombinations between the (^{4}S) and (^{2}D) terms occur in the group of lines observed, so that a separate analysis is required in order to determine the fine structures in the (^{2}D) series limit terms. The object of this paper is to give an account of the fine-structure analysis of twelve of these terms. The line transitions studied are shown in figure 1, from which it is seen that most of the terms are involved more than once. The concordance between the values of the fine-structure interval factors when calculated from more than one line serves therefore as an indication of the reliability of the values found.

In the (^{4}S) terms all the lines examined except one are transitions between $5p^3ns$ and $5p^36p$. The largest interval factor for a $5p^36p$ term is 25 cm$^{-1}\times10^{-3}$, whilst the two important s terms $6\,^5S_2$ and $7\,^3S_2$ have interval factors of 100 and 26 respectively. Hence a number of the structures are easy to analyse because the

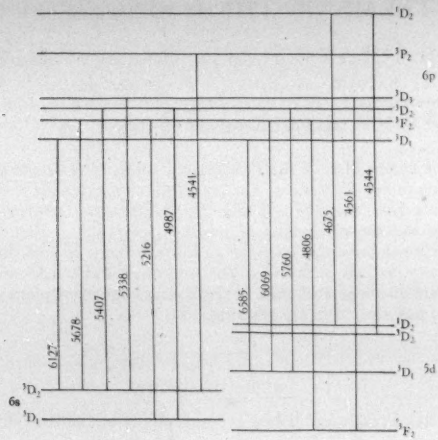

Figure 1. Line transitions involving (^{2}D) series limit terms.

upper and lower interval factors have a large ratio. The (^{2}D) terms are somewhat different; most of the structures are irregular and imperfectly resolved. This is due both to the approximate equality of the upper and lower interval factors in many cases, and to the fact that many of the lines lie in the blue, where the instrumental resolution has fallen off.

§ 2. OBSERVATIONS

The measurements are taken from the author's previous publication[1]. Since new allocations are known, the structures of the lines which have been classified and also analysed are shown in table 1. The lines indicated by an asterisk are those analysed here, and in these both the terms go to the (^{2}D) limit. The other lines involve the (^{4}S) limit and have already been analysed, but are included to complete the table.

§ 3. ANALYSIS

It is apparent from most of the structures that the interval factors in both the terms of a line are of the same order, a fact which makes analysis difficult and in some cases ambiguous. As the nuclear spin is 5/2, each line has a large number of components, e.g. a frequently occurring transition for which $\Delta J=2\rightarrow2$ has thirteen components, so that if the two interval factors are similar the blending can become

Table 1. Fine structures in the classified lines of the I^+ spectrum

Wave-length	Classification	Structure ($cm^{-1} \times 10^{-3}$) violet								
6585·0*	$5d\,^3D_1$–$6p\,^3D_1$	0 (2)	47 (6)	178 (3)	256 (2)					
6127·4*	$6s\,^3D_2$–$6p\,^3D_1$	0 (10)	200 (6)	234 (4)	354 (2)	432 (4)	535 (3)	618 (1)	645 (2)	
6068·8*	$5d\,^3D_1$–$6p\,^3F_2$	0 (2)	35 (3)	126 (10)	251 (4)	308 (15)				
5950·1	$6s\,^3S_1$–$6p\,^3P_1$	0 (3)	47 (3)	121 (2)	204 (4)					
5920·7	$6p\,^3P_0$–$7s\,^3S_1$	Single								
5787·1	$6p\,^3P_2$–$7s\,^3S_1$	0 (4)	56 (1)	106 (2)	149 (2)					
5774·7	$5d\,^3D_2$–$6p\,^5P_1$	0 (5)	741 (4)	1291 (3)	1686 (2)	1913 (1)				
5760·4*	$5d\,^3D_1$–$6p\,^3D_2$	0 (10)	56 (3)	100 (5)	132 (4)	159 (4)				
†5678·0*	$6s\,^3D_2$–$6p\,^3F_2$	0 (1)	86 (3)	173 (10)	238 (4)	293 (3)	424 (3)	482 (6)		
5625·7	$6s\,^3S_1$–$6p\,^3P_2$	0 (2)	28 (2)	70 (3)						
5504·8	$6s\,^3S_1$–$6p\,^3P_0$	0 (1)	33 (1)							
5496·8	$6s\,^5S_2$–$6p\,^5P_1$	0 (5)	429 (4)	756 (3)	991 (2)	1141 (1)				
5464·8	$6s\,^5S_2$–$6p\,^5P_2$	0 (10)	303 (1)	363 (4)	415 (2)	630 (3)	680 (3)	840 (2)	868 (3)	969 (3)
5407·3*	$6s\,^3D_2$–$6p\,^3D_2$	0 (16)	182 (8)	226 (7)	363 (6)	423 (6)	528 (2)	572 (4)	659 (4)	
5338·2*	$6s\,^3D_2$–$6p\,^3D_3$	0 (1)	107 (8)	236 (6)	348 (4)	429 (2)	461 (1)			
5216·2*	$6s\,^3D_1$–$6p\,^3F_2$	0 (3)	22 (1)	79 (3)	122 (4)	199 (5)	283 (6)	366 (12)		
5161·2	$6s\,^5S_2$–$6p\,^5P_3$	0 (5)	397 (4)	695 (3)	905 (2)	1025 (1)				
5156·4	$6p\,^5P_1$–$7s\,^5S_2$	0 (2)	75 (3)	163 (4)	266 (5)	382 (6)				
4987·0*	$6s\,^3D_1$–$6p\,^3D_2$	0 (4)	38 (3)							
4806·4*	$5d\,^3F_2$–$6p\,^3F_2$	0 (4)	53 (5)	121 (5)	168 (6)	213 (6)	252 (12)	293 (2)		
4675·5*	$5d\,^1D_2$–$6p\,^1D_2$	0 (12)	150 (4)	295 (10)	365 (20)	508 (4)	673 (3)			
4632·4	$6s\,^5S_2$–$6p\,^3P_2$	0 (5)	399 (4)	695 (3)	928 (2)	1054 (1)				
4561·0*	$5d\,^3F_2$–$6p\,^3D_3$	0 (1)	- - - - - - - - -		228 (4)					
4544·3*	$5d\,^3D_2$–$6p\,^1D_2$	0 (3)	240 (2)	373 (5)	685 (1)					
4540·9*	$6s\,^3D_2$–$6p\,^3P_2$	0 (2)	110 (1)	162 (1)						
4488·8*	$5d\,^3D_1$–$6p\,^3D_1$	0 (2)	117 (1)	162 (1)						

† Previously given as 5679·0 by mistake.

so serious that the interpretation is difficult. There are two lines in which the resolution is good and in which the upper interval factors are reasonably small compared with the lower term, namely λ 6127·4 and λ 5407·3. λ 6127·4 is $6s\,^3D_2 - 6p\,^3D_1$ and as the upper term has $J=1$ the line shows a simpler structure than λ 5407·3, for which $\Delta J = 2 \rightarrow 2$.

The analysis of this line, which has been carried out with a reasonable degree of precision, is shown in figure 2. The lower interval factor is 66·6, and although the upper is 28 the small value of J for the upper term produces a simplification in the pattern. Figure 3 shows the analysis of λ 5407·3 and the agreement between the

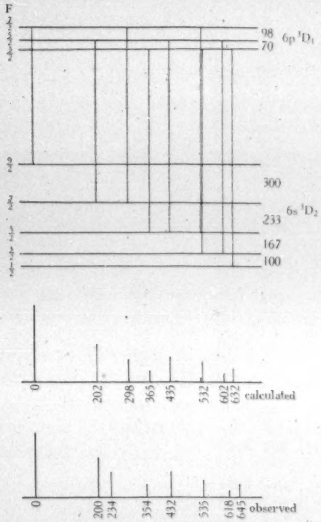

Figure 2. λ 6127·4.

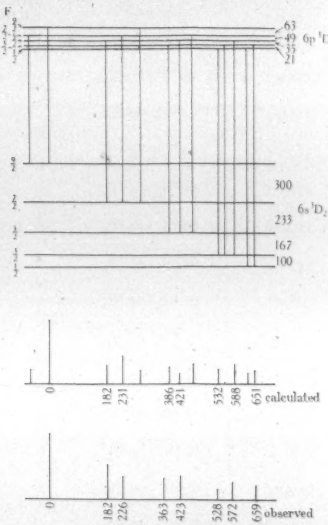

Figure 3. λ 5407·3.

calculated and observed patterns is reasonably good. In both cases the discrepancies are probably due to the difficulty of measurement.

It is important to notice that these analyses, which, as in the case of the (^{4}S) lines, have been carried out by the Fisher-Goudsmit method[5], presuppose the validity of the interval rule. It has been shown in the previous work on the fine structures in the arc and spark spectra of iodine that perturbations occur in some terms, and this fact must be considered in dealing with the present case. If a term is perturbed with a breakdown in the interval rule it is still possible to obtain an approximately correct value for the interval factor, but in the Fisher-Goudsmit diagram some components will be out of place.

Owing to the incompleteness of the resolution of the structures and also to the probable occurrence of deviations from the interval rule occasioned by perturbation,

the interval factors found for a given term vary somewhat when calculated from different lines. In quite a number of the lines analysed a component was found to be displaced. The following examples show the degree of variation in the calculated interval factors. Both λ 6127·4 and λ 5407·3 give 66·6 as the interval factor, henceforth denoted by A, for $6s\,^3D_2$ and approximately the same value is found from $\lambda\lambda$ 5678·0, 5338·2, 4540·9 which also involve this term. For the term $6p\,^3F_2$ the three lines $\lambda\lambda$ 5678·0, 5216·2, 4806·4 give A as $\sim$ 47, 40, 36 respectively. Thus 40 may be taken as an approximate value, the error being about 10 per cent. The values for A for $6p\,^3D_2$ given by λ 5407·3 and λ 4987·0 are both equal to 14. The line λ 5338·2 gives $A = \sim 27$ and λ 4561·0 gives $A = \sim 22$ for the term $6p\,^3D_3$. The former value

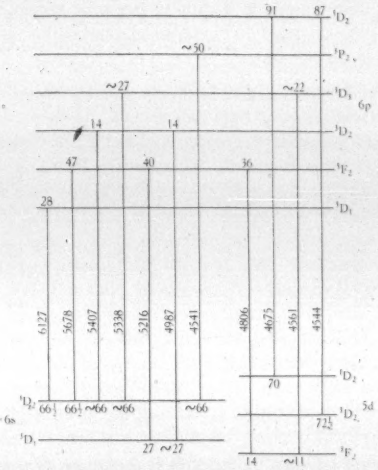

Figure 4. Interval factors calculated for each line transition.

is considered the more reliable, so that A is taken as $\sim$25 for this term. One more example will be quoted and that is the upper term $6p\,^1D_2$, which has the largest interval factor observed for the (^{2}D) terms. λ 4675·5 and λ 4544·3 both exhibit moderately wide structures, and although the region is not one which gives very high resolution with a silvered Fabry-Perot interferometer, the values found for A for the term in question are 91 and 87 respectively. The mean value, 89, is probably close to the true value.

The three lines $\lambda\lambda$ 6585·0, 6068·8, 5760·4 are of interest, for it was found impossible to fit these into Fisher-Goudsmit patterns. All involve $5d\,^3D_1$ as the lower term. This lower term must therefore be very strongly perturbed. An approximate estimate for A shows that it probably lies between 25 and 40.

It should be mentioned that a very faint component which had only been suspected in λ 5216·2 is probably non-existent, the analysis showing that it is

superfluous. It had been previously recorded as a line of strength 1, only 75 units away from a line of strength 24.

Figure 4 shows the line transitions which have been analysed, and at the ends of each line the interval factors calculated for that line are indicated. Line transitions are only schematic and not to scale.

§ 4. DISCUSSION OF RESULTS

All the interval factors now known for the I^+ spectrum are collected together in table 2. The degree of accuracy is much higher in the (^{4}S) terms than in the (^{2}D) terms, the error varying from 1 to 5 per cent in the former whilst in the latter the interval factors are only known to within 10 per cent except in the three largest values, which are fairly accurate. In the terms marked with a sign of approximation the error may exceed 10 per cent.

Table 2. Interval factors in the I^+ spectrum ($cm^{-1} \times 10^{-3}$)

(^{4}S)		(^{2}D)	
$6s\ ^5S_2$	100	$6s\ ^3D_1$	27
$7s\ ^5S_2$	26	$6s\ ^3D_2$	$66\frac{1}{2}$
$6s\ ^3S_1$	$5\frac{1}{2}$		
$7s\ ^3S_1$	Small		
$6p\ ^5P_1$	10	$6p\ ^3P_2$	~ 50
$6p\ ^5P_2$	~ 20	$6p\ ^1D_2$	89
$6p\ ^5P_3$	10	$6p\ ^3D_1$	28
$6p\ ^3P_0$	0	$6p\ ^3D_2$	14
$6p\ ^3P_1$	~ 25	$6p\ ^3D_3$	~ 25
$6p\ ^3P_2$	11	$6p\ ^3F_2$	40
$5d\ ^3D_2$	166	$5d\ ^1D_2$	~ 70
		$5d\ ^3D_1$	(?) 25–40
		$5d\ ^3D_2$	72
		$5d\ ^3F_2$	14

An important point revealed by the table is that many of the $6p$ and $5d$ electron terms have very large interval factors relative to those of the $6s$ electron terms. According to the usual assumptions it is not to be expected that the $6p$ and $5d$ electrons should be equal in penetrating power to the $6s$ electron, hence the implication is that the $5p^3$ group contributes to the value of the interval factor to an appreciable degree. A similar effect was observed in the p^4 groups of the iodine and bromine arc spectra.

The difference between the $6p$ terms belonging to the (^{4}S) and (^{2}D) systems is due to the rearrangement of the $5p^3$ group, and as there is a marked difference in the interval factors of the two sets of $6p$ terms it is apparent that the $5p^3$ group makes an important contribution. The electron coupling is partially *jj*, as is shown by the irregularity of the multiplets, so that $5p_{\frac{1}{2}}$ electrons will exist, and as a $p_{\frac{1}{2}}$ electron may behave in a heavy atom as if it were partially penetrating, moderately large nuclear coupling can exist for the $5p^3$ group. Thus the experimental values for the $6p$ terms fit in with expectation.

The most outstanding fact shown by the table is that most of the $5d$ electron terms have large interval factors, in fact the largest yet observed belongs to this group. It is very unlikely that a $5d$ electron can exhibit even partial penetration. Even if pure jj coupling is assumed there will then exist $d_{3/2}$ and $d_{5/2}$ electrons, and at most the $d_{3/2}$ electron will be comparable in penetrating power with a $p_{3/2}$ electron, so that the coupling will be very small. The large interval factors can be explained, however, as a perturbation effect. There are two types of perturbation. In the first, observed by Shenstone and Russell[6], two terms which are produced by different electron configurations, have the same L, S, J, and are both odd or both even, can perturb each other even if they are many thousands of cm^{-1} apart. In a perturbation of this type the wave functions characteristic of both the electrons mix, so that if one of the perturbing terms has a very wide fine structure associated with it the other term partakes of this property and also acquires a wide fine structure, the width depending upon the degree of perturbation. The interval rule holds accurately in such perturbed fine structures, only the value of the interval factor being determined by the perturbation. The second type of perturbation, which was found by Schüler and Jones[7] in Hg I and also occurs in the iodine arc spectrum, is due to the accidental close approach of two terms. In this type the fine-structure interval rule is broken in at least one of the terms if the values of J differ.

The (^{2}D) $5d\,^3D_1$ perturbation is doubtless of the second kind, for the interval rule appears to be broken. On the other hand the large values of the other $5d$ terms are due probably to perturbations of the first kind. Consider first (^{4}S) $5d\,^3D_2$ with the interval factor 166. The table shows that this large interval factor is not due to the $5p^3$ group, for $6s\,^5S_2$, in which the $6s$ electron is of most importance, has an interval factor of only 100. As the factors for $7s\,^5S_2$ and $6s\,^5S_2$ are 26 and 100 respectively, it is reasonable to expect that a $5s$ electron would produce an interval factor of at least 400 and even possibly much more. The normal state of I$^+$ is $5s^2 5p^4$, the $5d\,^3D_2$ term being produced by a displacement of a $5p$ electron to a $5d$ orbit. However the $5s^2$ shell can be broken, giving $5s\,5p^5$, $5s\,5p^4 6s$, $5s\,5p^4 6p$, etc., each term containing an unpaired $5s$ electron so that there are very large interval factors in many of the terms. Moreover as the coupling is neither LS nor jj the perturbation selection rule as to L and S will not be rigidly obeyed, for strictly speaking these vectors have no real meaning in such a case. It is very probable that one of these terms perturbs (^{4}S) $5d\,^3D_2$, and because the interval factor of the perturbing term is so large a value of 166 can easily result for (^{4}S) $5d\,^3D_2$ even if the terms are of the order of say 40,000 cm^{-1} apart, which is the order of the energy required to break up $5s^2$.

It may be noted that the interval rule is still accurately obeyed after perturbation, and the measurements show this to be so. An analogous case of an increase in interval factor associated with a $5d$ electron was found by the author[8] in the Sn II fine structures. Here the $5s^2 5d\,^2D_{5/2}$ term has an interval factor 130 whilst that of $5s^2 6s\,^2S_{1/2}$ is 207. The perturbation effect is no doubt similar.

The large interval factors in the (^{2}D) $5d$ electron terms are probably due in part to perturbation and in part to the contribution of the $5p^3$ group which appears to

have a larger coupling constant when going to the (^{2}D) limit than when going to the (^{4}S) limit. However there seems to be strong evidence of perturbation. The large interval factor for (^{2}D) $6p\,^1D_2$ implies a perturbing mechanism similar to that producing the large interval factor in (^{4}S) $5d\,^3D_2$. The same is perhaps true for (^{2}D) $5d\,^1D_2$ and (^{2}D) $5d\,^3D_2$.

§ 5. ACKNOWLEDGMENTS

I wish to express my thanks to Dr R. Peierls for helpful discussion on the question of perturbations. I wish also to take this opportunity of thanking Prof. W. L. Bragg, F.R.S., for the admirable experimental facilities granted me whilst I was carrying out this work.

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ABSOLUTE INTENSITIES IN THE SPECTRUM OF A LOW-PRESSURE QUARTZ MERCURY-VAPOUR DISCHARGE BURNER

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ABSTRACT. Absolute intensities of the main wave-lengths between 6000 and 2400 A. emitted by a commercial type of a very low-pressure mercury-vapour discharge burner are tabulated, and some theoretical aspects of the results as compared with those for high-pressure arcs are considered. Therapeutic effects of the two types of burner are discussed with reference to the production of erythema.

§ 1. INTRODUCTION

In a recent paper[1] values for the absolute intensities of the main wave-lengths in the mercury arc spectrum were given for high-pressure arcs, i.e. arcs where the vapour pressure of the mercury is of the order of 1 atmosphere. Various designs of mercury-vapour burner are made; they operate at pressures ranging between this high value and a fraction of a millimetre, i.e. with the tube barely warm. Burners of the latter type, which is often referred to as the "cold quartz" type, are useful therapeutically as they may be placed in contact with the skin without fear of temperature burns.

We present below data obtained on such a low-pressure type of burner, the vapour pressure being of the order of 0·01 mm. The discharge in tubes of this type takes place between cold metallic electrodes, the tubes operating with a moderately high-voltage a.-c. supply. For this particular type about 600 volts is required to initiate the discharge and about 300 volts to maintain it, sufficient leakage reactance being provided in the step-up transformer to stabilize the current. The tube passes 150 mA., so that the power in the discharge is only 45 watts in this case.

§ 2. PROCEDURE

Direct measurements with a spectroradiometer are not possible for these very low-pressure sources, as the intensities of all lines, except the resonance line, are very weak. The results given herewith were obtained by a spectrophotometric method whereby two magnesium-oxide screens were illuminated, one by the test source placed 100 cm. (the standard distance for which intensities are quoted) away, and the other by a standard high-pressure arc whose intensities for all the main wave-lengths had been carefully determined by the spectrometric method described in the previous paper[1]. The intensity of radiation on the magnesium-

oxide screen was varied in known manner by moving this standard source to various distances along the optical bench and deducing the actual intensity at the screen by means of the inverse-square law and the calibration values for one fixed distance. Radiation falling on the two magnesium-oxide screens then entered a spectrograph with a Hüfner rhomb before the collimator slit, and in this way juxtaposed spectra were obtained on the photographic plate. From these spectra records of equal photographic density were obtained and hence the intensities of the test source were deduced from the known values for the standard.

§ 3. RESULTS AND DISCUSSION

The results obtained are given in table 1. As is to be expected, the resonance line 2536·5 A. is very intense since the mercury-vapour pressure is so low that absorption in the outer layers of the vapour and self-reversal are practically absent. It will be noted that this line is 98 times as intense as the line at 4358 A. and accounts for 90 per cent of the total output of all the lines measured. Thus the intensity in the visible region of the spectrum is no guide to that in the short-wave ultra-violet.

Table 1. Radiant energy flux (μW./cm.^{2}) at 1 metre from the centre of quartz mercury-vapour burners

Wave-length (A.)	A.-c. discharge type. 300 V. 150 mA., very low pressure	A.-c. high-pressure arc type. 3·6 A. to common cathode
5780	0·17	38·2
5461	1·05	41·6
4358	1·20	35·3
4047	0·47	20·2
3650	0·65	56·0
3342	0·04	6·1
3132	0·71	40·3
3022	0·07	16·0
2967	0·22	9·1
2894	0·05	4·6
2804	0·02	6·5
2753	0·03	—
2652	0·07	16·1
2536	120·0	19·9
2482	0·03	5·1
Total	125	314
Total for λ 3132 and shorter wave-lengths	121	117

We have not determined the intensity of so many lines as in the high-pressure arcs; we obtained values for only the first two members of the sharp series and the first three of the diffuse series. However, when the logarithm of the intensity is plotted as before against wave-number, figure 1, the members of the diffuse series show a linear relation in contrast to the curves given in figure 4 of the previous paper[1] for the high-pressure arc. Hence Hulburt's[2] theoretical relation is fol-

lowed closely, at least by these few lines, in the low-pressure mercury discharge. This indicates that his probability function α is constant for the lines of a series under these conditions. The general agreement in the slopes of the sharp series, and the greater slopes of the several diffuse series found in the high-pressure arcs, are still maintained in this low-pressure discharge, and from these slopes we deduce

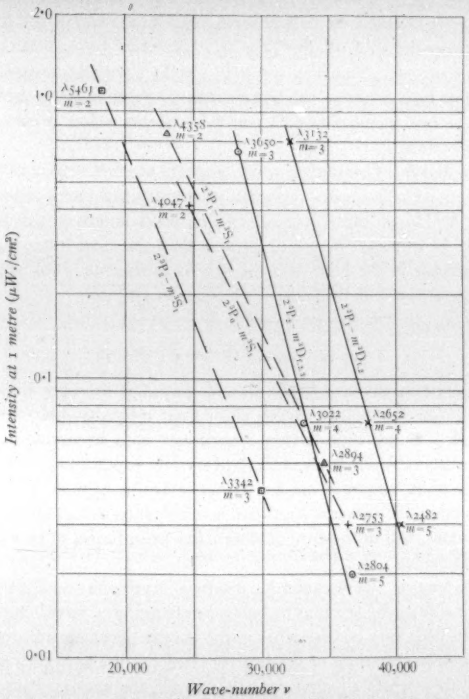

Figure 1. Relation between intensity and wave-number for the sharp and diffuse series of the mercury spectrum in low-pressure discharge.

approximate values of 5900° K. and 3500° K. for the temperatures of the excited atoms in the $2\,^3S$ and $2\,^3D$ levels respectively. McAlister's[3] relations for his lower-pressure arc show a tendency towards a more linear relation. On the basis of the current and voltage ratings of his burners the vapour pressure in McAlister's determinations would be intermediate between the pressure in the high-pressure arcs of the previous paper[1] and the low pressure of the discharge burner used in the present investigation. It appears, then, that with increase of vapour pressure,

departure from the theoretical relation becomes more marked, especially for lines in the diffuse series.

From a comparison of figure 1 and figure 4 of the previous paper[1] it will be seen that, as the vapour pressure of the mercury changes from a low to a high value, the relative intensity-distribution throughout the spectrum changes. Thus, whereas at low pressure the $2\,^3P_2 - m\,^3D_{1,2,3}$ series ($\lambda\lambda$ 3650, 3022, 2804, ...) is relatively weaker than series having as their first members λ 3132, λ 4358 and λ 5461, at high pressure the intensities of all the lines in this series have increased until it is relatively the strongest. Similarly the $2\,^3P_1 - m\,^3D_{1,2}$ series increases relatively in intensity until, at high pressure, the first member, λ 3132, is comparable in intensity with λ 5461, the first member of $2\,^3P_2 - m\,^3S_1$, whereas at low pressure it was only 68 per cent as intense.

It will be noted that this source, which appears to emit weakly as judged by the visible output, is actually quite a powerful source of ultra-violet radiation of wave-length 2536·5 A. The absolute intensity of that wave-length in this burner, which consumes only 45 watts in the arc, is greater than the total intensity of $\lambda\lambda$ 2536·5 and 2534·8 together in the high-pressure 3·5-A. burner no. 160, which consumes 495 watts in the arc; it is in fact nearly 1·6 times as intense.

§ 4. THERAPEUTIC EFFECTS

It is of interest to see how the high and very low-pressure mercury burners compare as regards therapeutic effects, since their intensity-distribution is so different, the high-pressure type having a spectrum with numerous strong lines of more or less comparable intensity, and the very low-pressure type emitting practically the whole of its output in one very intense line at 2536 A. We shall consider only the production of erythema, since this is often taken as a guide for treatment in many clinical cases, and in the cure of rickets has been found to be a close guide to the results obtainable.

Only wave-lengths below 3200 A. produce erythema, and even these vary greatly in their effect, the maximum being produced at a wave-length of 2967 A. Although individuals vary considerably in the energy necessary to produce reddening of the skin, determinations of the relative effects of the various wave-lengths by several individual workers all agree reasonably well, the greatest divergence occurring at the shorter wave-lengths. Such determinations have been made by Hausser[4], by Luckiesh, Holladay and Taylor[5] and by Coblentz, Stair and Hogue[6], and the mean of the results obtained by these various experimenters are given in figure 2, which shows the relative erythemal effectiveness referred to unit effect at λ 2967 A. In other words, the curve shows the effectiveness which each wave-length would have in producing a minimum perceptible erythema if it were of the same intensity as λ 2967. Hence from this curve we can obtain the equivalent intensity of λ 2967 for any source if we have determined the intensities of the various spectral lines in absolute value by multiplying these values by the corresponding erythemal effectiveness and summing the results. The sources are then directly comparable in respect

not only of their absolute intensity but also of their effectiveness in producing erythema.*

The wave-lengths 3132, 3022, 2967, 2894, 2804, 2652, 2536, 2482 A., of which 3132, 2652 and 2536 are understood to include groups, are those most responsible in the mercury spectrum for production of erythema. For these wave-lengths we have a total power of 268μW./cm^2 at 100 cm. from the high-pressure 2·5-A. burner no. 844, whilst the low-pressure burner gives 121μW./cm^2 at the same distance. This latter burner has thus 0·45 times the total intensity of the former. However, by the process described above, it is found to be 0·6 times as effective as regards the production of erythema, owing almost exclusively to the intense line at 2536 A.

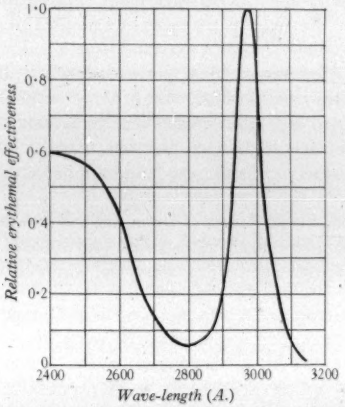

Figure 2. Relative effectiveness of various wave-lengths in producing erythema.

In fact, in a therapeutic aspect, this low-pressure discharge burner can be considered as a source of monochromatic radiation of wave-length 2536 A.

Data obtained with an a.-c. high-pressure type of mercury-vapour burner with two anodes and a common mercury-pool cathode are also given in table 1 for comparison. It will be noted that the total intensity of wave-lengths below 3200 A. for this burner and for one of the low-pressure discharge type are comparable, the radiation from the discharge burner being 1·1 times as intense for these wave-lengths though only 0·4 times as intense if all wave-lengths are considered. However, on the basis of effectiveness in producing erythema, calculation of the product of absolute intensity-values and the relative values given in figure 2 shows that the low-pressure burner would be 1·4 times as effective.

Experimental confirmation of this conclusion was obtained by exposing the inner, upper (untanned) arm first to the low-pressure burner and then, adjacently,

* Erythema, in the sense in which we use it in this discussion, is taken to be the minimum perceptible erythema, often referred to as "M.P.E."

to the high-pressure burner for a graded series of exposure-times and at a distance of 100 cm. in each case. Minimum perceptible erythema was produced in 3 minutes by the low- and in 4 minutes by the high-pressure burner, showing the former to be 1·3 times as effective in producing erythema. This result is in sufficiently good agreement with the calculated value of 1·4. Direct comparison made, as above, on the same person on neighbouring areas of skin and at about the same time are reliable.

Data on the total energy of λ 2967 or its equivalent required to produce minimum perceptible erythema is meagre, and the results obtained by two groups of experimenters show a wide divergence although amongst the three individuals of each group the results were in fair agreement. Thus Luckiesh, Holladay and Taylor[5] give 4300 μW.-sec./cm.^{2} as the mean of a number of determinations made on these three workers, whilst Coblentz, Stair and Hogue[7] give 20,500 μW.-sec./cm.^{2} as their mean value. However, different parts of the body and different persons react differently to ultraviolet radiation, and it is not surprising that marked differences are obtained in any experimental determinations of this nature. It is probable that these two sets of data can be taken, more or less, as limits between which the energy required to produce the minimum perceptible erythema on any one person might lie.

The exposures made by the author of 3 minutes and 4 minutes for the low- and high-pressure burners under consideration correspond to about 11,500 μW.-sec./cm.^{2} of radiation of wave-length 2967 A., or about the mean of the two sets of data referred to above.

§ 5. ACKNOWLEDGMENTS

These investigations were carried out in the Laboratories of the Thermal Syndicate Ltd. on their standard types of quartz mercury-vapour burners, and the author wishes to thank this firm for permission to publish the paper.

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EXPERIMENTS ON CONDUCTING LAMINAE IN PERIODIC MAGNETIC FIELDS

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ABSTRACT. The secondary magnetic field due to conducting circular discs, placed in a spatially uniform magnetic field which alternates with time, has been measured and it has been found that as the dimensions of the disc, the conductivity, and the frequency increase, the secondary field also increases and the phase-difference between the secondary field and the primary field changes from $\pi/2$ to 0. Simple considerations show that these features appear for all conductors or conducting laminae of similar shape, no matter how they are excited. The results have been applied to the practical case of the location of good conducting mineral lodes beneath the earth's surface.

§ 1. INTRODUCTION

One method of geophysical prospecting[1] consists in inducing currents in good conducting bodies, such as metal sulphides, by the application of an alternating magnetic field, the presence of the conductor being detected by the secondary magnetic field set up by the currents induced. Although small-scale experiments on this method have been carried out by several observers, either they have been conducted with types of bodies which do not approximate in shape to those occurring in the field, or sufficient detail has not been given in the published results. Thus Slichter[2] has performed experiments on conducting spherical shells placed in the field due to a loop and has compared his results with those calculated for such a body placed in a uniform field. Sundberg[3], on the other hand, has determined the field due to rectangular sheets excited by an alternating current flowing in a rectangular loop, thus reproducing approximately the conditions obtaining in practice. Full details of the latter experiments are not given and it is impossible to determine from them the factors which control the secondary field due to the body.

The following experiments were made with the object of determining the above factors. Various circular discs, placed with their planes perpendicular to a spatially uniform magnetic field alternating with time, were used to represent the conducting deposit in the applied magnetic field. To some extent this is open to the objection which applies to Slichter's results, but since mineral deposits approximate closely to sheets rather than to spheres or spherical shells, the results throw light on the magnitude of the distortion of the magnetic field due to such bodies and on the factors upon which the response depends, particularly the thickness, resistivity and frequency. To some extent, by using discs of different radii, the effect of the linear dimensions of the sheet has been investigated.

The uniformity of the applied magnetic field was essential to ensure that all discs, no matter what their dimensions, should be excited in the same way, while the circular shape of the metal plates was chosen because, by using the fact that the field is the same at points equidistant from the axis, search coils with large effective areas could be designed readily to measure the radial field. With any non-symmetrical shape it would be necessary to construct search coils whose dimensions were small compared with the dimensions of the plate and the distances involved, so that the measured field could be assumed uniform throughout the search coil.

§ 2. EXPERIMENTAL ARRANGEMENT

The uniform field was produced by means of two large square loops of side 213·5 cm. joined in series and placed with their planes parallel and 116·3 cm. apart. This system, which forms a modified Helmholtz system, has been described by Rankine[4] as a means of obtaining the most uniform field by means of square coils.

a, b If $2a$ is the side of the square and $2b$ the separation of the coils, the most uniform field is obtained if $a/b = 1{\cdot}837$. In the system used $a/b = 1{\cdot}836$. If the centre of the

x, y coil system is taken as the origin of coordinates, the axes Ox, Oy parallel to the sides

z, H_0 of the coil and Oz perpendicular to them, then if H_0 is the field at the origin, the field at various points near the origin is as shown in table 1.

Table 1

Position	Field
$(0, 0, 0)$	H_0
$(\pm 0{\cdot}22a, 0, 0)$	$0{\cdot}99902\ H_0$
$(0, \pm 0{\cdot}22a, 0)$	$0{\cdot}99902\ H_0$
$\left(\pm \frac{0{\cdot}22}{\sqrt{2}} a, \pm \frac{0{\cdot}22}{\sqrt{2}} a, 0\right)$	$0{\cdot}99952\ H_0$
$(0, 0, \pm 0{\cdot}22a)$	$0{\cdot}99815\ H_0$

It will be seen that over a circle of radius $0{\cdot}22a$ (in this case 23·5 cm.) in the XOY plane, in which the disc lies, the field is constant to within one part in 1000. The maximum radius of the discs was 23·1 cm., and as the apparatus used was not capable of measuring to the above accuracy, the discs were assumed to be in a uniform field. The coil system was connected directly to the generator by twisted flex leads, which did not produce any appreciable magnetic field at the centre of the system. In the test, the current used was about 8 A. at 532 c./sec., giving a primary field of amplitude 0·062 oersted, or about 10 A. at 50 c./sec., giving a field of amplitude 0·077 oersted.

The apparatus used for measuring the field was originally designed for actual inductive prospecting[5], and required only slight modification for small-scale work. The circuit for the work at 532 c./sec. is shown in figure 1. The search coil A, fixed in position relatively to the square Helmholtz coil system HH and threaded by the field due to it, supplies currents differing in phase by $\pi/2$ to the two potentiometers R, S. By varying the resistance X, the phase-difference between the currents in R

and S and the magnetic field at A can be changed until the e.m.f. set up in the search coil B, placed in the normal uniform field of the Helmholtz system, is balanced entirely on the scale R, the scale S being at its central zero. The instrument with this adjustment is direct-reading, and in the presence of a metal disc the readings on R and S give measures of the distorted field in phase and in quadrature with the applied field. For the work at 50 c./sec. it was necessary to change the constants of the potentiometer, and owing to the difficulty of designing a suitable search coil to replace A at the lower frequency the phase-calibration could not be performed. This meant that the instrument was no longer direct-reading, but the in-phase and quadrature components of the distortion due to the discs could be readily calculated from the readings. Calculation showed that at both frequencies the field at the

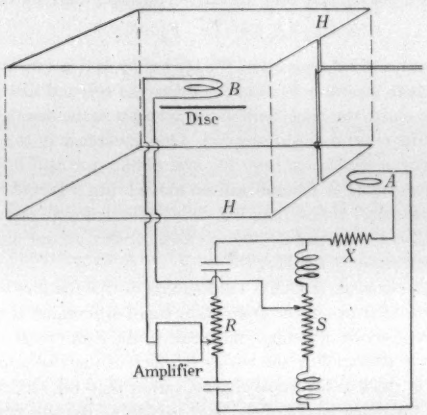


Figure 1.

centre of the square coil system due to the currents flowing through the fixed coil A was much less than 0·1 per cent of the main field and could be neglected in comparison with it.

The metal disc rested on three wooden levelling-screws passing through a heavy wooden base, and its position was fixed in relation to the frame carrying the search coil by two wooden stops mounted on the base and contacting with the circumference of the disc. These stops consisted of suitable wooden screws passing through wooden blocks and they permitted the centre of the disc to be moved through a small range. The framework carrying the search coil was also mounted on the base and allowed the coil to be moved along the axis of the disc. In the construction of the mounting for the disc and search coil all metal was avoided so that the applied field was undistorted by the parts in question.

The field on the axis of the disc was measured by a small coil having 770 turns wound in a groove 0·6 cm. wide, 0·4 cm. deep and of mean radius 2·7 cm. The coil

was first placed in the position of the disc and the phase calibration performed, the reading on the in-phase scale giving a measure of H_0, the applied field. At all other positions the readings were taken with and without the metal disc, and from them the distortion due to the disc was calculated as a fraction of the applied field.

The measurements of the radial field were made with suitable coils placed parallel to and coaxial with the disc and moved to different distances from the disc. The coils lay in two identically similar grooves, with a mean separation of 1 cm., cut in the same wooden former. Coils with the same number of turns were wound in each groove and connected in opposition, so that, when they were placed in a uniform field, the resultant e.m.f. induced in the system was zero. In any other field, if

F_1, F_2 F_1 is the inward normal flux over the base, F_2 the outward normal flux over the top,

F_3 and F_3 the outward normal flux over the curved surface, then, by Gauss's theorem,

$$F_1 - F_2 - F_3 = 0 \quad \text{or} \quad F_3 = F_1 - F_2.$$

As the coils are connected in opposition, the induced e.m.f. is a measure of $(F_1 - F_2)$, and hence the system measures F_3 directly. When the coil and disc are parallel and coaxial, F_3 will be due to the radial field of the currents in the disc at a distance from the axis equal to the mean radius of the coil. One advantage of these coils is that a slight displacement of the centre from the axis of the disc will not introduce any serious error, for one part of the coil will be moved into a greater radial field and another part into a weaker field. Since $\partial H_r/\partial r$ is the same for all points on the rim of

H_r the coil, where H_r is the radial field, the increase of flux on one side will be compensated by a decrease on the other.

It was found, in general, that coils constructed in this manner were not exactly astatic. Slight dissimilarities in the grooves, or small differences in the windings of the coils themselves, result in a small difference in the mean radii of the two component windings. Consequently the curved surface of the coil approximated to a

θ section of a cone of small semivertical angle θ, rather than the section of a cylinder.

H_a If H_r and H_a are the radial field and the field parallel to the axis respectively, then

$$F_3 = (H_r \cos\theta + H_a \sin\theta)\, A \doteq (H_r + H_a\theta)\, A$$

A when A is the effective area of the curved sides. When the coil is rotated through 180° about a diameter, the second term changes sign and the mean of the two observations eliminates the unwanted effect. The constants of the six coils used in the measurement of the radial field are given in table 2.

Table 2

Coil	Mean radius r (cm.)	No. of turns n	A (cm.^{2} × 10^4)
A	4·6	450	1·31
B	7·1	300	1·35
C	11·3	200	1·41
D	14·8	150	1·40
E	18·8	120	1·41
F	22·6	100	1·42

A is the area of the curved surface of the coil and $= 2\pi rnh$, where h is the mean separation of the two windings. As before, the potentiometer has been calibrated with a coil of known effective area placed in the normal applied field, and the distortion due to the discs is expressed in terms of the applied field. h

§ 3. EXPERIMENTAL RESULTS

The dimensions of the discs and their resistivities, obtained from measurements on specimens cut from the same sheet, are as shown in table 3.

Table 3

	Radius a (cm.)	Thickness d (cm.)	Resistivity ρ (e.m.u.)	d/ρ
Copper I	20·3	0·210	$2{\cdot}94.10^3$	$7{\cdot}14.10^{-5}$
Copper II	20·4	0·0475	$1{\cdot}73.10^3$	$2{\cdot}75.10^{-5}$
Brass	20·3	0·198	$6{\cdot}56.10^3$	$3{\cdot}02.10^{-5}$
Lead	20·3	0·342	$2{\cdot}21.10^4$	$1{\cdot}55.10^{-5}$
German silver I	23·1	0·0924	$2{\cdot}47.10^4$	$3{\cdot}76.10^{-6}$
German silver II	20·3	0·0924	$2{\cdot}47.10^4$	$3{\cdot}76.10^{-6}$
German silver III	17·8	0·0924	$2{\cdot}47.10^4$	$3{\cdot}76.10^{-6}$

a, d, ρ

The field on the axis of all seven discs was measured at 532 c./sec. and for the first five at 50 c./sec., but the radial field was obtained for copper I and lead at 532 c./sec. only. Typical examples of these fields are shown in figures 2, 3 and 4. In these diagrams the in-phase components are given by the continuous curves, the broken lines referring to the quadrature components. Some of the observations are shown on the curves to indicate the accuracy of the measurements, but in many cases, to avoid confusion, the observed values have been omitted. Figure 2 shows the in-phase components I_r and the quadrature components Q_r of the radial field, expressed as a fraction of the applied field H_0, as measured with the coils in table 2 at various distances from the disc. It will be seen that the quadrature components are approximately between 0·3 to 0·5 of the in-phase components. Similar curves were obtained for copper I. In this case the maxima on the in-phase curves were displaced to a greater radial value and were larger than the maxima for the lead disc. The quadrature components were much smaller, the maximum measured value of Q_r/H_0 being 0·09, and in general they were about 0·1 of the in-phase components. With the aid of these and similar curves the complete radial fields have been depicted by lines of equal in-phase and equal quadrature component, figure 3. Figure 3*a*, in which the in-phase lines only are shown since the quadrature values were too small to be plotted accurately, refers to the copper, and figure 3*b* refers to the lead. It will be seen that, in general, the field at a given point is greater for the copper than for the lead, while the maxima for the copper are at a greater distance from the axis, illustrating the tendency for the current to concentrate nearer the rim of the better conductor. I_r, Q_r

Examples of the axial field are given in figure 4 for copper I, copper II and lead at 532 c./sec. and at 50 c./sec. Comparing the magnitude of the in-phase com-

ponents I_a/H_0 and the quadrature components Q_a/H_0 of the axial field for lead at 532 c./sec., we can see that they are of the same order as the corresponding ratio for the radial field, figure 2, a result which was confirmed by the measurements on copper I. This is to be expected, since outside the disc the components may be

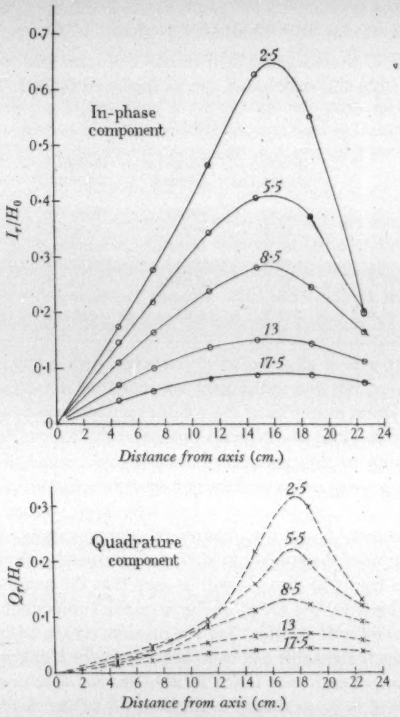


Figure 2. Radial field due to lead disc. The figures attached to the curves refer to the distance (cm.) from the disc.

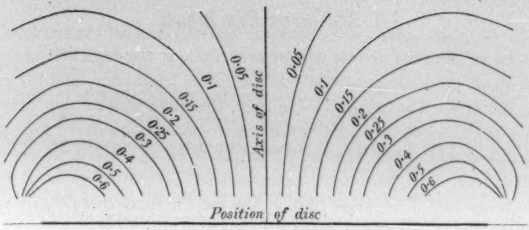
Ω, r derived from a potential Ω which, on the axis and at a distance r from the disc, has the form

$$\Omega = \Sigma\,(Ar^n + B/r^{n+1}),$$

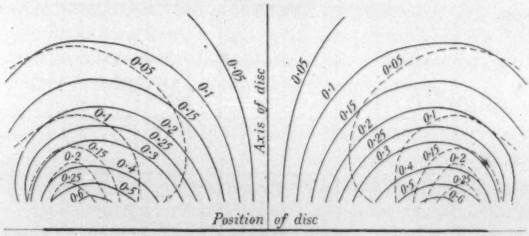
and at a point (r, θ, ϕ) off the axis

$$\Omega = (Ar^n + B/r^{n+1})\,P_n\,(\cos\theta),$$

differing only by the introduction of the Legendre coefficient $P_n\,(\cos\theta)$. Accordingly, the factors controlling the magnitudes of the two components may be determined from an examination of the axial field only.



(*a*) Copper disc.



(*b*) Lead disc.

Figure 3. Radial field due to copper I and lead at 532 c./sec. The radius of I_r/H_0 and Q_r/H_0 are denoted by the figures attached to the curves.

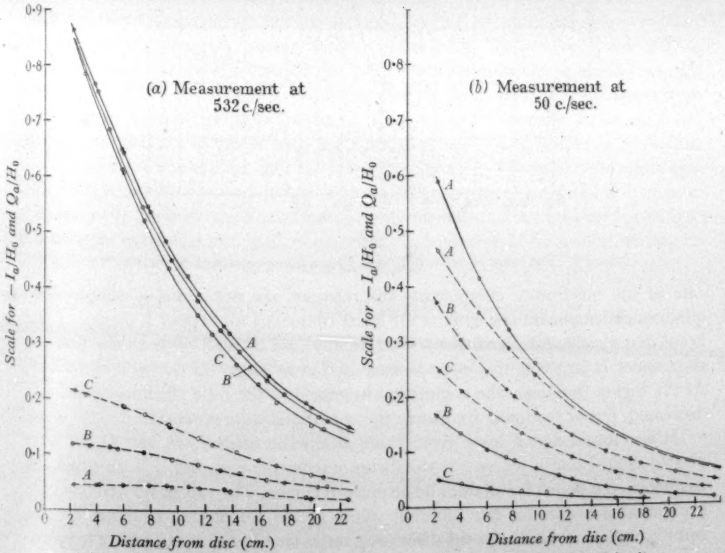

(a) Measurement at 532 c./sec.
(b) Measurement at 50 c./sec.
Scale for $-I_a/H_0$ and Q_a/H_0
Distance from disc (cm.)
A
B
C
0 2 4 6 8 10 12 14 16 18 20 22
0·1 0·2 0·3 0·4 0·5 0·6 0·7 0·8 0·9

Figure 4. Axial field due to conducting discs, *A*, copper I; *B*, copper II; *C*, lead.

In the case of the axial field it will be seen that, at the high frequency, the in-phase component predominates, while at the lower frequency, and for the poorer conducting sheets such as copper II and lead, the quadrature component is larger than the in-phase component. In all cases the in-phase component for a given disc decreases considerably as the frequency changes from 532 c./sec. to 50 c./sec., and at a given frequency the component decreases with decreasing value of the ratio of thickness to resistivity. The values of this ratio for the three discs shown in figure 4 are for copper I, $7{\cdot}14.10^{-5}$; for copper II, $2{\cdot}75.10^{-5}$; and for lead, $1{\cdot}51.10^{-5}$. In the

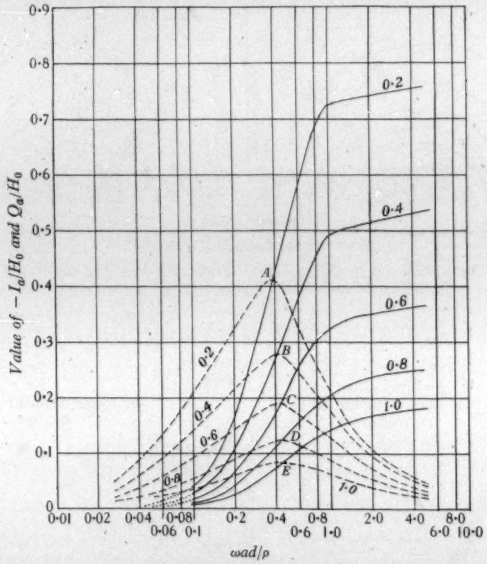


Figure 5. The value of z/a is indicated by the figures attached to the curves.

case of the quadrature components the relations are not quite so simple. The quadrature component is greater at the lower frequency for copper I, copper II and brass, but smaller for German silver I. In the case of lead, close to the disc the component is larger at the lower frequency, but at larger distances it is smaller. At the higher frequency the component increased as the ratio thickness/resistivity decreased, but at the lower frequency the conditions were reversed.

z It was found that if for a given value of z/a the fields I_a/H_0 and Q_a/H_0 were
ω plotted against $\omega ad/\rho$, where z is the distance from the disc and ω is 2π times the frequency, the points for all discs lie on smooth curves. The values derived from the experimental results for five different values of z/a are plotted in figure 5. For convenience, since $\omega ad/\rho$ for the discs used varies from 0·027 up to 4·86, a logarith-

mic scale has been used for this quantity. It will be seen that below 0·04 the in-phase component is negligible compared with the quadrature component. Between the values of 0·1 and 1·0 the in-phase component increases rapidly, and thereafter an increase in the parameter $\omega ad/\rho$ produces little effect, and presumably each curve tends to a limiting value corresponding to the effect of a perfect conductor. The quadrature curves rise to maxima as $\omega ad/\rho$ increases, and then fall away rapidly. It will be seen that the intersections A, B, C, D and E of corresponding in-phase and quadrature curves occur at the maxima of the quadrature curves. Thus, below 0·4 the quadrature components are greater and for sufficiently low values of the parameter the secondary field is entirely in quadrature with the applied field. Above 0·4 the in-phase field predominates, and for sufficiently large values of $\omega ad/\rho$ the distortion is entirely in-phase with the applied field.

§ 4. DISCUSSION OF RESULTS

These curves reproduce the same characteristics as other bodies when placed in a uniform field if the response is plotted against a suitable parameter. In the case of a sphere of radius a, the parameter[2, 6] is $\omega a^2/\rho$, while for a spherical shell of radius a and thickness d the parameter[2, 6] is $\omega ad/\rho$. Even with a simple loop it is easy to show that a field changing in the same manner will be obtained if the secondary field at a given point is plotted against ω/R, where R is the resistance of the circuit. Elementary considerations show that these features are to be expected for a conductor of given shape, when the distortion is plotted against a suitable parameter involving the resistivity, frequency and size of the body. The two factors controlling the magnitude and distribution of the induced currents in the conductor are the resistivity and the opposition to change of the magnetic field. For bodies of high resistivity or for low frequencies the resistivity is the important factor, and the induced currents are in phase with the induced e.m.f. $-j\omega N$, where N is the flux through a closed line of flow, and are proportional to $1/\rho$. For good conductors and high frequencies the second factor is the more important and roughly increases proportionally to the frequency. Consequently the induced currents are in quadrature with the induced e.m.f. and are practically independent of frequency, leading to in-phase fields which tend to a saturation value. *N*

§ 5. APPLICATION OF THE PRINCIPLE OF SIMILITUDE

The parameter controlling the secondary field may be obtained more precisely from the electromagnetic equations. With electromagnetic units

$$\text{Curl } E = -\mu \dot{H},$$

$$\text{Curl } H = \frac{4\pi}{\rho} E,$$

where E and H are the electric and magnetic fields, μ is the permeability and ρ is the resistivity. These equations lead to *E, H, μ*

$$\frac{\partial^2 R}{\partial x^2} + \frac{\partial^2 R}{\partial y^2} + \frac{\partial^2 R}{\partial z^2} = \frac{4\pi\mu}{\rho} \frac{\partial R}{\partial t},$$

R where R is any component of the electric or magnetic field. For bodies of similar
α shape, let α be the length of a line in the body, i.e. a measure of its linear dimensions, and let the coordinates be expressed in terms of this length. Thus

$$x=\xi\alpha, \quad y=\eta\alpha, \quad z=\zeta\alpha,$$

and hence

$$\frac{\partial^2 R}{\partial\xi^2}+\frac{\partial^2 R}{\partial\eta^2}+\frac{\partial^2 R}{\partial\zeta^2}=\frac{4\pi\mu\alpha^2}{\rho}j\omega R \qquad \text{.....(1),}$$

since, in the case of alternating fields, when a steady state has been reached, $\partial/\partial t$ may be replaced by the operator $j\omega$. Consequently

$$R=F\left(\frac{4\pi\mu\alpha^2 j\omega}{\rho},\ \xi,\ \eta,\ \zeta\right) \qquad \text{.....(2),}$$

and the parameter controlling the response is $\omega\mu\alpha^2/\rho$, corresponding to $\omega\alpha^2/\rho$ which obtains for the case of the sphere. Equation (2) involves the principle of similitude first pointed out by C. V. Drysdale[7], for to reproduce the field in a particular case on a different scale $\omega\mu\alpha^2/\rho$ must be a constant. Since the wave-length λ of an electromagnetic disturbance in a medium is $\sqrt{(\rho/2\pi\omega\mu)}$, the principle of similitude requires that the wave-length of the disturbance shall be changed by the same factor as the other linear dimensions.

Equation (2) is not directly applicable to the case of the discs here used because they are not bodies of similar shape, i.e. a/d is not a constant. For laminae of the same shape but differing in thickness d and in α, a measure of the surface dimensions, the following equation holds outside the lamina:

$$\frac{\partial^2 R}{\partial\xi^2}+\frac{\partial^2 R}{\partial\eta^2}+\frac{\partial^2 R}{\partial\zeta^2}=0 \qquad \text{.....(3),}$$

in virtue of equation (1), since $\rho=\infty$. If the lamina lies in the XOY plane it can be shown that[8]

$$\frac{4\pi d}{\rho}\cdot\frac{\partial H_{z1}}{\partial t}=\frac{4\pi d}{\rho}\cdot\frac{\partial H_{z2}}{\partial t}=\left|\frac{\partial H_z}{\partial z}\right|_1^2,$$

where the suffixes 1 and 2 refer to points close to the boundary on each side of the sheet. Hence, since $z=\alpha\zeta$ and $\frac{\partial}{\partial t}=j\omega$,

$$\frac{4\pi j\omega\alpha d}{\rho}H_{\zeta 1}=\frac{4\pi j\omega\alpha d}{\rho}H_{\zeta 2}=\left|\frac{\partial H_\zeta}{\partial\zeta}\right|_1^2 \qquad \text{.....(4),}$$

from which, in combination with equations (3) and (4), it would appear that the field is of the form

$$R=F\left(\frac{4\pi j\omega\alpha d}{\rho},\ \xi,\ \eta,\ \zeta\right),$$

which agrees with the experimental results obtained with the discs, and with the result quoted for the spherical shell. One feature of the above analysis is that the exact nature of the exciting field is not specified and thus the general results can be applied to bodies not in uniform fields.

§6. CONCLUSIONS

Three inferences of great practical importance to the application of the inductive methods of locating well-conducting subterranean bodies may be drawn from these results. In the first case there is no simple phase relation between the secondary field and the applied field, and the field instruments must be capable of dealing with all phase conditions. With the resistivities and dimensions of bodies available in practice, it is probable that only the smaller values of $\omega\varkappa d/\rho$ are important and, although in this range the quadrature components predominate, the in-phase component may be an appreciable fraction of the total field. It also appears that, for a body of given surface dimensions, exactly the same field will be obtained for all combinations of resistivity and thickness as long as the ratio remains constant. Thus a bed of clay of resistivity 500 Ω.-cm. and thickness 100 cm. will be indistinguishable from a copper-sulphide body of resistivity 100 Ω.-cm. and thickness 20 cm.

The fact that the secondary field increases with frequency does not imply that, in the practical case, a body will be more readily detected if a higher frequency is used, for another factor enters into the problem. The surrounding rocks have a finite resistivity, usually much greater than the resistivity of a sulphide body, and accordingly induced currents are set up in those rocks, giving rise at the surface to a secondary field which forms a background on which local effects are superimposed. The primary field is thus decreased by absorption occurring in the rocks that lie between the body and the surface, and the absorption increases as the resistivity decreases or the frequency increases. For the secondary field at the surface due to the body there are two opposing factors, the primary field decreasing with frequency and the response increasing with frequency. Consequently there is an optimum frequency for a given body which will yield the best results. An increase in the frequency beyond the optimum value will result in a smaller indication on an increased background, while a decrease in the frequency will reduce both the local anomaly and the background, the former being reduced by the greater factor. The optimum frequency will decrease with increasing depth of the body and also with decrease of resistivity of the intervening medium. In the case of a large surface conductivity, the optimum frequency may be so small that the field at the surface due to the body will be negligible compared with the applied field. Under these conditions the inductive method is at a marked disadvantage, which it shares with other methods employing alternating currents.

§7. ACKNOWLEDGMENTS

In conclusion I wish to thank Prof. A. O. Rankine for the interest he has taken in this work and also the Department of Scientific and Industrial Research, whose grant to the Applied Geophysics Department of the Royal College of Science rendered this work possible.

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AN OPTICAL CALIBRATION PROBLEM

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ABSTRACT. Suitable measures are obtained for the uncertainty, corresponding to a fixed error of phase, in the object-image relation of a symmetrical optical instrument. For a thin lens with its aperture stop in contact with the lens the uncertainty is proportional to the distance between the object and the image. The formulae are utilized to determine the most accurate values of the coefficients in the object-image relation from observations including many pairs of co-ordinates.

The results given by the phase criterion, unlike those derived by a purely geometrical treatment, are unaltered if the object and image spaces are interchanged.

In the course of optical experiments it is sometimes required to determine the connexion between conjugate points for part of the optical train without disturbing this portion of the apparatus. The procedure followed is to attach to the apparatus scales on which corresponding positions u, u' of an object and its image can be read. These observations have then to be fitted to a formula of the type

$$Auu' - Bu' - Cu + D = 0 \qquad \ldots\ldots(1).$$

Three pairs of points suffice to give a solution, but it is usual to observe a greater number. In general each set of three will then yield different values of the ratios $A:B:C:D$, and the method of selecting mean values deserves attention. Obviously comparatively little weight can be assigned to determinations from close sets of points. For such sets the minors of

$$\begin{vmatrix} u_1u_1' & u_1' & u_1 & 1 \\ u_2u_2' & u_2' & u_2 & 1 \\ u_3u_3' & u_3' & u_3 & 1 \end{vmatrix}$$

will be small, but it does not follow that we shall reach a satisfactory result by merely adding corresponding minors, for by this procedure if any observation were included with u or u' indefinitely great this single observation alone would determine the ratio of B or C to A irrespective of all the others. From the nature of the arrangement we cannot avoid this difficulty by adopting an expression which involves only the reciprocals of u and u'. Indeed the fact that a small change in one reading may correspond to a large change in the other should put us on our guard against accepting any treatment which does not take into account the physics of the problem.

It is now widely recognized that the correct measure of errors of focus is the difference of path, as utilized in the late Lord Rayleigh's treatment of somewhat similar problems. In the question we are considering it may be assumed that the extreme path differences will be obtained by comparing axial and marginal paths.

If the inclination of the extreme rays to the axis is of moderate magnitude, and u and u' are assumed to increase as the distances from the lens of the object and image respectively increase,* the marginal path will exceed the axial path by T,† where

$$2AT=(B-uA)(M^2+N^2)-2(MM'+NN')+(C-u'A)(M'^2+N'^2)\ldots(2),$$

and M, N and M', N' are the direction cosines of a marginal ray with respect to axes perpendicular to the axis of the system. The corresponding intersection distances in the u and u' planes of this ray are given by the equations

$$Ay=(B-uA)M-M', \quad Ay'=M-(C-u'A)M',$$
$$Az=(B-uA)N-N', \quad Az'=N-(C-u'A)N'.$$

Similarly if the aperture is limited by a stop corresponding to one of the scale readings $u=s$, $u'=s'$, and the intersection points in the stop plane are η, ζ or η', ζ', we shall have

$$A\eta=(B-sA)M-M', \quad A\eta'=M-(C-s'A)M',$$
$$A\zeta=(B-sA)N-N', \quad A\zeta'=N-(C-s'A)N'.$$

Considering now light from an object point on the axis, so that $y=z=0$, we obtain

$$M=\frac{\eta}{u-s}=\frac{-\eta'}{Aus'-Bs'-Cu+D}=\frac{M'}{B-uA},$$
$$N=\frac{\zeta}{u-s}=\frac{-\zeta'}{Aus'-Bs'-Cu+D}=\frac{N'}{B-uA},$$

where we have assumed the relation $BC-AD=1$ in deriving the values involving η' and ζ'. Substituting these values of the direction cosines in (2) we obtain

$$\frac{2T}{\eta^2+\zeta^2}=\frac{(B-uA)(Auu'-Bu'-Cu+D)}{(u-s)^2},$$

or

$$\frac{2T}{\eta'^2+\zeta'^2}=\frac{(B-uA)(Auu'-Bu'-Cu+D)}{(Aus'-Bs'-Cu+D)^2}.$$

Both these equations may be expressed in a single form. If we put

$$Auu'-Bu'-Cu+D=d,$$

$-d$ is the optical interval between the planes selected (with some small error) as corresponding conjugate planes. If the stop is in the object space, $u-s$ is the separation between the object and the stop plane, and if the stop is in the image space $-d_s$ is the corresponding optical interval, where $Aus'-Bs'-Cu+D=d_s$. In the first case the real and the optical intervals are identical; we may accordingly denote either of these optical intervals by $-d_s$. Moreover $B-uA$ is the reciprocal of the magnification m which the object undergoes in the system we are considering. We therefore have in all cases

$$\frac{2T}{r^2}=\frac{d}{md_s^2} \qquad \ldots\ldots(3),$$

where r is the radius of the effective stop.

* The conventions are those of Group II, Case 1, described in the *Report on the Teaching of Geometrical Optics*, The Physical Society, 1934.

† Hamilton's notation for one of his auxiliary characteristic functions is adopted.

The asymmetry in this formula is due to our having definite knowledge of agreement of phase at the object, but not in the approximate image plane. If however we neglect errors in focus except in the factor d itself, we can immediately convert (3) into the symmetrical form

$$\frac{2T}{rr'}=\frac{2T}{\eta\eta'+\zeta\zeta'}=-\frac{d}{d_s d_s'} \qquad \ldots\ldots(4),$$

where $-d_s'$ is the optical interval between the image plane and the image of the real stop plane, i.e. d_s' has one of the values $-(u'-s')$, $Au's-Bu'-Cs+D$, the choice depending upon whether the real stop is in the object or the image space.

An important special case of (4) arises when the effective stop is in a principal plane. We then have $r'=r$, the relation connecting conjugate points is

$$A+\frac{1}{d_s}+\frac{1}{d_s'}=0,$$

and the formula reduces to

$$\frac{2T}{Ar^2}=-\frac{d}{\mathscr{D}} \qquad \ldots\ldots(5),$$

where $\mathscr{D}$ is the overall distance between object and image planes less the actual distance between the principal planes. For a thin lens the principal planes are coincident, and for many systems their separation is negligible, so that $\mathscr{D}$ may be taken with sufficient accuracy to be the distance apart of the object and image.

We see therefore that, corresponding to a given standard of accuracy in focussing, the tolerance in d is proportional to md_s^2, or with sufficient accuracy to $d_s d_s'$, and that it will often be the case, with the stop in or near to a principal plane, that the tolerance is proportional to $\mathscr{D}$, the distance apart of the object and image.

A practical procedure is to compute provisional values of A, B, C, D from a mean and the two extreme positions of object and image. With these values of the constants compute values of d for all the observations, and then evaluate either d/md_s^2 or $d/d_s d_s'$ or $d/\mathscr{D}$. If the distribution of these quantities is not systematic as regards sign and the largest positive and largest negative values are of equal magnitude, the values of A, B, C, D obtained may be accepted as satisfactory. Otherwise from these quantities we pick out four which are judged to have the largest outstanding errors from a mean curve, these being alternately positive and negative as u increases.* Distinguish these outstanding observations by the suffixes 1, 2, 3, 4. Assume, for the purpose of illustration, that $\mathscr{D}$ is a suitable measure of the tolerance to be permitted, and that $\mathscr{D}_1$, $\mathscr{D}_2$, $\mathscr{D}_3$, $\mathscr{D}_4$ are the values of $\mathscr{D}$ for the four observations. Then the equation which fits the observations best is

$$\begin{vmatrix} uu' & u' & u & 1 & 0 \\ u_1u_1' & u_1' & u_1 & 1 & \mathscr{D}_1 \\ u_2u_2' & u_2' & u_2 & 1 & -\mathscr{D}_2 \\ u_3u_3' & u_3' & u_3 & 1 & \mathscr{D}_3 \\ u_4u_4' & u_4' & u_4 & 1 & -\mathscr{D}_4 \end{vmatrix} = 0 \qquad \ldots\ldots(6).$$

* For a discussion of the principle adopted see "The mid-course method of fitting a parabolic formula of any order to a set of observations", *Proc. phys. Soc.* **46**, 560 (1934).

When the best relative values of A, B, C, D have been obtained their absolute values, if required, are found by dividing each by $(BC-AD)^{\frac{1}{2}}$. The resolution of the ambiguity of sign offers no difficulty in practice. If the scales are arranged differently it may happen that the dividing factor will be $(AD-BC)^{\frac{1}{2}}$. In any event the factor is real, and the sign will be chosen to give the correct sign for A. For details see the reference on p. 76.

$\mathscr{D}_1$, $\mathscr{D}_2$, $\mathscr{D}_3$ and $\mathscr{D}_4$ may be regarded as weights attached to the determinations of A, B, C, D when the pairs of points 1, 2, 3, 4 respectively are omitted. The determinant (E say) obtained by deleting the first row and last column from (6) measures the magnitude of the outstanding errors. For if we denote by A_p, B_p, C_p, D_p the coefficients found when points p are omitted, alternations of sign being avoided, we have

$$E=\begin{pmatrix} u_1u_1' & u_1' & u_1 & 1 \\ u_2u_2' & u_2' & u_2 & 1 \\ u_3u_3' & u_3' & u_3 & 1 \\ u_4u_4' & u_4' & u_4 & 1 \end{pmatrix} \begin{pmatrix} A_1 & -A_2 & A_3 & -A_4 \\ -B_1 & B_2 & -B_3 & B_4 \\ -C_1 & C_2 & -C_3 & C_4 \\ D_1 & -D_2 & D_3 & -D_4 \end{pmatrix}$$

and

$$\frac{A}{\Sigma\mathscr{D}_pA_p}=\frac{B}{\Sigma\mathscr{D}_pB_p}=\frac{C}{\Sigma\mathscr{D}_pC_p}=\frac{D}{\Sigma\mathscr{D}_pD_p}=\frac{Au_pu_p'-Bu_p'-Cu_p+D}{-(-)^pE\mathscr{D}_p}$$

$$=\frac{1}{(\Sigma\mathscr{D}_pB_p\Sigma\mathscr{D}_pC_p-\Sigma\mathscr{D}_pA_p\Sigma\mathscr{D}_pD_p)^{\frac{1}{2}}}=\frac{1}{(\Sigma\mathscr{D}_p\Sigma\mathscr{D}_p\Delta_p-\Sigma\mathscr{D}_p\mathscr{D}_q\Delta_{pq})^{\frac{1}{2}}} \quad \ldots\ldots(7),$$

where $$\Delta_p=B_pC_p-A_pD_p$$

and $$\Delta_{pq}=(B_p-B_q)(C_p-C_q)-(A_p-A_q)(D_p-D_q).$$

Δ_p can be expressed as the product of six factors, and Δ_{pq} as the product of four factors, but it will usually be unnecessary to evaluate them directly.

The quality of the observations can be determined from the values of T when the final values of A, B, C, D are inserted in one of the equations (3), (4) or (5). According to Lord Rayleigh T should lie within the limits $\pm\lambda/4$ for sensibly perfect definition, where λ is the equivalent wave-length of the light used. In our problem we interpret this tolerance as fixing the limits of sensibly perfect focussing.

It may be observed that, as with other questions of this class, the results reached by means of limits depending on path differences disagree with those derived geometrically by assuming that the definition will appear satisfactory if the rays intersect an image plane in an area less than a fixed limiting size. It is not difficult to show that this assumption leads to tolerances in d proportional to d_s. It should be noted that, unlike the results given earlier, this conclusion is essentially unsymmetrical as regards the object and image spaces, so that if object and image are interchanged the distribution of tolerances on this basis will be altered.

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ON THE COMBINATION OF OBSERVATIONAL DATA

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ABSTRACT. A method is devised for solving the following problem: Given m curves derived by m different experimenters to describe the same physical process, how are these to be combined into one unique curve? Formulae are developed that enable the ordinates of the combined curve to be calculated simply from those of the constituent members.

SUPPOSE that m experimenters each separately investigating a particular process produce m sets of data or m curves each purporting to describe the same phenomenon quantitatively. How are these separate curves to be combined? Can any criterion be developed that enables us to decide what weight to attach to each of the individual members of the system in combining them?

It seems clear that such weights must be associated with the extent to which each one of the sets correlates as a whole with every other set, in addition to the extent to which any particular reading is in partial agreement with other corresponding readings. A direct and unconditioned use of the method of least squares would not take these considerations into account. We commence with the case of two sets of data.

(1) Let $(A_1, \ldots A_n)$ and $(B_1, \ldots B_n)$ be two sets of observations obtained by two different experimenters to represent variations in the same phenomena at positions $(x_1, \ldots x_n)$ not necessarily evenly spaced. We assume that no errors arise in determining $x_1, \ldots x_n$, that the values of the As and Bs are almost entirely determined by the nature of the subject-matter investigated, and that the differences between A_1 and B_1, A_2 and B_2, etc. arise only from experimental errors. It follows that the A and B series should be highly correlated. The problem is to derive from these observations a third series $Y_1, Y_2, \ldots Y_n$ at $x_1, x_2, \ldots x_n$ which *correlates most highly with* (A) *and* (B). This last phrase is taken to mean that if r_{ay} and r_{by} be the correlation coefficients between the As and the Ys and between the Bs and the Ys respectively, then the Ys are to be chosen to make a homogeneous symmetrical function a maximum.

A_n, B_n

x_n

Y_n

r_{ay}, r_{by}

(2) Let M_A, M_B, M_Y be the arithmetic means of the As, the Bs and the Ys. If α_s, β_s and η_s are deviations of A_s, B_s and Y_s each from its mean, then

M_A, M_B, M_Y

$\alpha_s, \beta_s, \eta_s$

$$\sum_1^n \alpha_s = \sum_1^n \beta_s = \sum_1^n \eta_s = 0,$$

$$r_{ab} = \frac{\Sigma \alpha_s \beta_s}{\sqrt{(\Sigma \alpha_s^2 . \Sigma \beta_s^2)}}, \quad r_{ay} = \frac{\Sigma \alpha_s \eta_s}{\sqrt{(\Sigma \alpha_s^2 . \Sigma \eta_s^2)}}, \quad r_{by} = \frac{\Sigma \beta_s \eta_s}{\sqrt{(\Sigma \beta_s^2 . \Sigma \eta_s^2)}}.$$

It will simplify our notation if we write

a_s, b_s, y_s

$$\frac{\alpha_s}{\sqrt{\Sigma \alpha_s^2}} = a_s, \quad \frac{\beta_s}{\sqrt{\Sigma \beta_s^2}} = b_s, \quad \frac{\eta_s}{\sqrt{\Sigma \eta_s^2}} = y_s.$$

Then

$$\sum_1^n a_s = \sum_1^n b_s = \sum_1^n y_s = 0,$$

$$\sum_1^n a_s^2 = \sum_1^n b_s^2 = \sum_1^n y_s^2 = 1,$$

$$r_{ab} = \sum_1^n a_s b_s; \quad r_{ay} = \sum_1^n a_s y_s; \quad r_{by} = \sum_1^n b_s y_s.$$

Thus the problem of determining the set (Y) that correlates most highly with the sets (A) and (B) can be expressed in terms of the sets (y), (a) and (b).

(3) We examine in the first place how far the set $(y_1, \ldots y_n)$ can be determined to make $F(r_{ay}, r_{by})$ a maximum where F is a given continuous homogeneous function of degree N.

F
N

For this we require

$$\delta F = \frac{\partial F}{\partial r_{ay}} \delta r_{ay} + \frac{\partial F}{\partial r_{by}} \delta r_{by} = 0 \qquad \ldots\ldots(1),$$

where

$$\delta r_{ay} = \Sigma a_s \delta y_s \quad \text{and} \quad \delta r_{by} = \Sigma b_s \delta y_s \qquad \ldots\ldots(2).$$

Thus inserting (2) in (1) we require

$$\sum_1^n \left(a_s \frac{\partial F}{\partial r_{ay}} + b_s \frac{\partial F}{\partial r_{by}} \right) \delta y_s = 0 \qquad \ldots\ldots(3).$$

In addition, from the restrictive conditions on y, we have

$$\sum_1^n y_s \delta y_s = 0, \quad \sum_1^n \delta y_s = 0 \qquad \ldots\ldots(4).$$

Combining (3) and (4) in the usual way we find that

λ, μ

$$\sum_1^n \left(a_s \frac{\partial F}{\partial r_{ay}} + b_s \frac{\partial F}{\partial r_{by}} + \lambda y_s + \mu \right) \delta y_s = 0,$$

where λ and μ are constants to be determined.

Equating coefficients of δy_s to zero we have

$$a_s \frac{\partial F}{\partial r_{ay}} + b_s \frac{\partial F}{\partial r_{by}} + \lambda y_s + \mu = 0 \quad (s = 1, \ldots n) \qquad \ldots\ldots(5).$$

Summing the set (5) and remembering that

$\Sigma a_s = \Sigma b_s = \Sigma y_s = 0$, we deduce that $\mu = 0$.

Multiplying (5) by y_s, summing and noting that

$$\Sigma a_s y_s = r_{ay}, \quad \Sigma b_s y_s = r_{by}, \quad \Sigma y_s^2 = 1,$$

we find

$$r_{ay} \frac{\partial F}{\partial r_{ay}} + r_{by} \frac{\partial F}{\partial r_{by}} + \lambda = 0.$$

Thus, since F is a homogeneous function of Nth degree, by Euler's theorem

$$\lambda = -NF.$$

Accordingly (5) takes the form

$$a_s \frac{\partial F}{\partial r_{ay}} + b_s \frac{\partial F}{\partial r_{by}} = y_s NF \quad (s = 1, \ldots n) \qquad \ldots\ldots(6).$$

Multiplying (6) by a_s and b_s respectively and summing we obtain

$$\left.\begin{aligned} \frac{\partial F}{\partial r_{ay}} + r_{ab} \frac{\partial F}{\partial r_{by}} &= r_{ay} NF \\ r_{ab} \frac{\partial F}{\partial r_{ay}} + \frac{\partial F}{\partial r_{by}} &= r_{by} NF \end{aligned}\right| \qquad \ldots\ldots(7)$$

Equations (6) and (7) between them serve to determine r_{ay}, r_{by} and y_s.

(4) Eliminating NF, $\dfrac{\partial F}{\partial r_{ay}}$ and $\dfrac{\partial F}{\partial r_{by}}$ between (6) and (7) we have

$$\begin{vmatrix} a_s & b_s & y_s \\ 1 & r_{ab} & r_{ay} \\ r_{ab} & 1 & r_{by} \end{vmatrix} = 0$$

or
$$y_s [1 - r_{ab}^2] = a_s [r_{ay} - r_{ab} r_{by}] + b_s [r_{by} - r_{ab} r_{ay}] \qquad \ldots\ldots(8).$$

Again associating Euler's identity

$$r_{ay} \frac{\partial F}{\partial r_{ay}} + r_{by} \frac{\partial F}{\partial r_{by}} = NF$$

with (7) and eliminating F we have

$$\begin{vmatrix} 1 & r_{ab} & r_{ay} \\ r_{ab} & 1 & r_{by} \\ r_{ay} & r_{by} & 1 \end{vmatrix} = 0$$

or
$$(1 - r_{ab}^2)(1 - r_{ay}^2) = (r_{by} - r_{ab} r_{ay})^2 \qquad \ldots\ldots(9).$$

For our purpose we shall be interested in the case where F is symmetrical in r_{ay} and r_{by}, in which case (7) implies that

$$r_{ay} = r_{by}.$$

Equation (9) then gives
$$r_{ay} = r_{by} = \sqrt{\frac{1 + r_{ab}}{2}} \qquad \ldots\ldots(10),$$

and (8)
$$y_s = (a_s + b_s)/\sqrt{\{2(1 + r_{ab})\}} \qquad \ldots\ldots(11).$$

Since it can easily be shown that $|r_{ab}| \leqslant 1$ and r_{ab} is positive for those cases with which we are concerned, it follows that y_s is in general slightly greater than the mean of a_s and b_s.

We have now to reinterpret these results in terms of the original set of data:

$$\text{Observed values} \begin{cases} x_1, & x_2, & x_3, \ldots x_n \\ A_1, & A_2, & A_3, \ldots A_n \\ B_1, & B_2, & B_3, \ldots B_n. \end{cases}$$

(5) Now
$$Y_s = M_Y + \eta_s = M_Y + \gamma y_s \qquad \ldots\ldots(12),$$

where M_Y and γ are still unknown.

Also
$$A_s = M_A + \alpha_s, \quad B_s = M_B + \beta_s.$$

We propose to determine M_Y and γ by the method of least squares. Thus we require

$$\sum_1^n [(Y_s - A_s)^2 + (Y_s - B_s)^2],$$

i.e.
$$\sum_1^n [(M_Y + \gamma y_s - M_A - \alpha_s)^2 + (M_Y + \gamma y_s - M_B - \beta_s)^2],$$

to be a minimum for variations in M_Y and γ. This leads easily to the two equations

$$M_Y = \tfrac{1}{2}(M_A + M_B) \qquad \text{.....(13),}$$

and
$$2\gamma \sum_1^n y_s^2 = \sum_1^n \alpha_s y_s + \sum_1^n \beta_s y_s,$$

or since
$$r_{ay} = r_{by},$$

or
$$2\gamma = r_{ay} (\sqrt{\sum_1^n \alpha_s^2} + \sqrt{\sum_1^n \beta_s^2}),$$

$$\gamma = \frac{\sqrt{n}}{2} r_{ay} [\sigma_A + \sigma_B] \qquad \text{.....(14),}$$

σ_A, σ_B where σ_A and σ_B are the standard deviations of the A and B series respectively.

Thus
$$Y_s = M_Y + \gamma y_s$$
$$= \tfrac{1}{2}(M_A + M_B) + \frac{\sqrt{n}}{2} r_{ay} [\sigma_A + \sigma_B] \frac{a_s + b_s}{\sqrt{2(1 + r_{ab})}}$$
$$= \tfrac{1}{2}(M_A + M_B) + \frac{\sqrt{n}}{4} [\sigma_A + \sigma_B] \left[\frac{\alpha_s}{\sqrt{\Sigma \alpha^2}} + \frac{\beta_s}{\sqrt{\Sigma \beta^2}} \right]$$
$$= \tfrac{1}{2}(M_A + M_B) + \tfrac{1}{4} [\sigma_A + \sigma_B] \left[\frac{\alpha_s}{\sigma_A} + \frac{\beta_s}{\sigma_B} \right] \qquad \text{.....(15),}$$

where M_A and M_B are the means of the As and Bs respectively, and the αs and βs are the deviations of these values from their means so that

$$A_s = M_A + \alpha_s, \; B_s = M_B + \beta_s.$$

Accordingly all the constants in the calculation of the series Y that correlates most highly with the two experimentally determined series A and B have now been determined.

Turning now to the general case of m sets (A), (B), (C), . . . we proceed with the analysis as before. Corresponding to equation (7) associated with Euler's identity we have

$$\frac{\partial F}{\partial r_{ay}} + r_{ab} \frac{\partial F}{\partial r_{by}} + r_{ac} \frac{\partial F}{\partial r_{ay}} = r_{ay} NF \qquad \text{.....(16),}$$

$$r_{ab} \frac{\partial F}{\partial r_{ay}} + \frac{\partial F}{\partial r_{by}} + r_{bc} \frac{\partial F}{\partial r_{ay}} = r_{by} NF \qquad \text{.....(17),}$$

$$r_{ac} \frac{\partial F}{\partial r_{ay}} + r_{bc} \frac{\partial F}{\partial r_{by}} + \frac{\partial F}{\partial r_{cy}} = r_{cy} NF \qquad \text{.....(18),}$$

$$r_{ay} \frac{\partial F}{\partial r_{ay}} + r_{by} \frac{\partial F}{\partial r_{by}} + r_{cy} \frac{\partial F}{\partial r_{cy}} = NF \qquad \text{.....(19).}$$

Also in the same way corresponding to equation (8)

$$\begin{vmatrix} a_s & b_s & c_s & y_s \\ 1 & r_{ab} & r_{ac} & r_{ay} \\ r_{ab} & 1 & r_{bc} & r_{by} \\ r_{ac} & r_{bc} & 1 & r_{cy} \end{vmatrix} = 0 \qquad \text{.....(20).}$$

Equations (16), (17) and (18) serve to determine r_{ay}, r_{by}, r_{cy} in any given case and as before equation (21) gives y_s as a linear combination of a_s, b_s and c_s. Unlike the case of two sets A and B, the precise values of these correlation coefficients for a larger number of sets appear to depend on the nature of the function F. The case of a linear function however leads easily to a solution. Here we have the sets of observed values (A), (B), (C),... and we have to determine the set (Y) to make the correlation function

$$F = r_{ay} + r_{by} + r_{cy} + \ldots \qquad \text{.....(21)}$$

a maximum.

Equations (16), (17) and (18) lead to

$$r_{ay} = (r_{aa} + r_{ab} + r_{ac} + \ldots) / \sqrt{\sum_{p,q=a,b,c,\ldots} \sum r_{pq}} \qquad \text{.....(22),}$$

where

$$r_{aa} = r_{bb} = \ldots = 1,$$

from which it easily follows that equation (20) leads to

$$y_s = (a_s + b_s + c_s + \ldots) / \sqrt{\sum_{p,q=a,b,c,\ldots} \sum r_{pq}} \qquad \text{.....(23).}$$

Once more writing

$$Y_s = M_Y + \eta_s = M_Y + \gamma y_s,$$

where M_Y is the mean of the terms in the Y set and applying the method of least squares we easily find, if there are m sets (A), (B), (C),..., that

$$M_Y = \frac{1}{m} (M_A + M_B + M_C + \ldots) \qquad \text{.....(24),}$$

and

$$m\gamma = \sum_1^n \alpha_s y_s + \sum_1^n \beta_s y_s + \ldots$$

$$= \sqrt{n} \, [r_{ay}\sigma_A + r_{by}\sigma_B + \ldots] \qquad \text{.....(25).}$$

Thus finally

$$\begin{aligned} Y_s &= M_Y + \gamma y_s \\ &= \frac{1}{m} [M_A + M_B + M_C + \ldots] \\ &\quad + \frac{\sqrt{n}}{m} [r_{ay}\sigma_A + r_{by}\sigma_B + \ldots] \, [a_s + b_s + c_s + \ldots] / \sqrt{\sum_{p,q=a,b,c,\ldots} \sum r_{pq}} \\ &= \frac{1}{m} [M_A + M_B + M_C + \ldots] \\ &\quad + \frac{1}{m} [r_{ay}\sigma_A + r_{by}\sigma_B +] \left[\frac{\alpha_s}{\sigma_A} + \frac{\beta_s}{\sigma_B} + \ldots \right] / \sqrt{\sum_{p,q=a,b,c,\ldots} \sum r_{pq}} \qquad \text{.....(26).} \end{aligned}$$

In the case of three sets (A), (B) and (C), for example, this may be written

$$Y_s=\frac{1}{3}(M_A+M_B+M_C)$$

$$+\frac{1}{3}\left(\frac{\alpha_s}{\sigma_A}+\frac{\beta_s}{\sigma_B}+\frac{\gamma_s}{\sigma_C}\right)\frac{\sigma_A+\sigma_B+\sigma_C+r_{ab}(\sigma_A+\sigma_B)+r_{bc}(\sigma_B+\sigma_C)+r_{ca}(\sigma_C+\sigma_A)}{3+2(r_{ab}+r_{bc}+r_{ca})} \quad \ldots\ldots(27).$$

We note that if all the sets show the same standard deviation, then the value of Y at each position is simply the mean of the separate ordinates.

The following table indicates the steps in the calculation and checks for n observations in each set.

Observations:

A_s	$\alpha_s=M_A-A_s$	α_s^2	α_s/σ_A		
—	—	—	—		
$\Sigma\div n=M_A$	$\Sigma=0$	$\Sigma\div n=\sigma_A^2$	$\Sigma=0$	$\sigma_A=\ldots$	
B_s	$\beta_s=M_B-B_s$	β_s^2	β_s/σ_B	$\alpha_s\beta_s/\sigma_A\sigma_B$	
—	—	—	—	—	
$\Sigma\div n=M_B$	$\Sigma=0$	$\Sigma\div n=\sigma_B^2$	$\Sigma=0$	$\Sigma\div n=r_{ab}$	$\sigma_B=\ldots$
C_s	$\gamma_s=M_C-C_s$	γ_s^2	γ_s/σ_C	$\alpha_s\gamma_s/\sigma_B\sigma_C$	$\beta_s\gamma_s/\sigma_B\sigma_C$

Formula (15) is to be used for two sets, and formula (27) for three. This formula is a particular case of (26) for any number.

548.74

THE EFFECT OF CRYSTAL-SIZE ON LATTICE-DIMENSIONS

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ABSTRACT. The lattice constants of the lithium, sodium and potassium halides have been determined by the method of electron-diffraction, gold and graphite being used as reference standards. It has been found that crystal-size can and does exert an appreciable effect upon the lattice-dimensions.

§ 1. INTRODUCTION

The use of zinc oxide as a reference material was advocated by Finch and Quarrell[1] in the determination of crystal-lattice constants by electron-diffraction. They took as constants those assigned by W. L. Bragg[2] to zincite. Later, however, Finch and Wilman[3] pointed out that more recent X-ray determinations of the constants of zincite and other specimens of specially pure zinc oxide differed, not only from Bragg's values, but also among themselves by as much as 1 per cent, and they therefore measured by electron-diffraction the lattice constants of zinc oxide prepared by the combustion of a zinc of forensic quality, gold leaf being used as reference standard. They obtained an axial ratio agreeing within the limits of experimental error with Bragg's value; their a and c values, however, exceeded not only Bragg's but also those due to all other X-ray investigators, by amounts which could certainly not be ascribed to errors in the measurement of diffraction-ring radii. It was shown furthermore that the discrepancy was not due either to thermal expansion or to charging-up effects, and the hope was then expressed that a redetermination might be carried out with X rays and condensed zinc-oxide smoke.

More recently it was suggested by one of us[4] that the apparent discrepancy between the values of the lattice constants of zinc oxide as determined by diffraction of X rays and electrons respectively might be explained in terms of a theory first put forward in 1930 by Lennard-Jones[5], according to whom the lattice-dimensions of crystals of homopolar compounds should increase with decreasing crystal size, whilst with ionic substances the reverse effect should occur.

X-ray experiments have been carried out by Lowry and Bozorth[6], Randall and Rooksby[7], Randall, Rooksby and Cooper[8], and K. A. and U. Hofmann[9], as a result of which it was suggested that in the case of certain glasses and carbons the lattice constants appeared to vary with the crystal-size in accordance with Lennard-Jones's theory. No certain conclusions could be drawn, however, because it was a question of detecting slight differences in the diameters of ill-defined haloes.

Owing to the far shorter wave-lengths available in electron-diffraction, it is quite easy to obtain a hundredfold increase in definition as compared with X rays when the overall dimensions of the diffracting crystals are less than about 100 A.[17] For this reason, and in order to put Lennard-Jones's theory to the test of experiment in the case of ionic compounds, determinations of the lattice constants of a series of alkali halides were carried out by the diffraction of high-speed electrons. Gold leaf was used and the results were checked by using the C—C spacing in the cleavage plane of graphite as a dimensional reference standard.

§ 2. EXPERIMENTAL

The camera was made in the Winnington Research Department of Messrs I.C.I. (Alkali) Ltd., from designs based on that of the instrument described elsewhere[10]. The cathode and camera sections were, however, separately evacuated by means of independent oil-vapour diffusion pumping systems, both backed by a high-speed rotary oil pump operating at about 0·01 mm. The diffusion pumps could be bye-passed by means of wide-bore Audco valves, an arrangement which permitted of opening the camera without cooling off the pumps and thus contributed greatly to an increased speed of operation.

Transmission patterns were recorded from specimens set up in one of the following ways: (i) Alkali halide was deposited on gold leaf, giving a composite diffraction pattern. (ii) Alkali halide or graphite was deposited on an amorphous collodion film supported on nickel gauze and gold supported on gold or nickel gauze. Double-shutter patterns were recorded in this case. (iii) The halide on collodion and that on gold were supported side by side and so close together on the same gauze that the electron beam, 0·1 mm. in diameter, passed through part of each specimen simultaneously and gave a composite alkali-halide and gold pattern.

The 24-ct. gold leaf supplied and guaranteed free from alloy by Messrs G. M. Whiley Ltd. was thinned in the usual manner by being floated on *N*/50 KCN solution and washed in several changes of distilled water. Samples of the leaves used in these experiments were double-shuttered with each other and also with specimens from the book originally used by Finch and Wilman in their determination of the lattice constants of zinc oxide. No difference could be detected in the corresponding lattice constants.

The lithium, sodium and potassium halides were the pure reagents supplied by Messrs Hopkins and Williams Ltd., mostly for analytical purposes. They were tested for those normally occurring impurities, other than waters of crystallization, the presence of which might be expected to affect the lattice constants. Thus, the sodium and potassium fluorides contained less than 0·05 and 0·2 per cent respectively of chlorides, and the sodium chloride less than 0·2 per cent of sulphate. The lithium and potassium salts gave the sodium flame test, but in no case was sodium present in sufficient amount for detection by precipitation as the dihydroxytartrate or zinc uranyl acetate. The potassium chloride was free from magnesium. Nitrates, bromides and iodides proved to be absent in the case of the

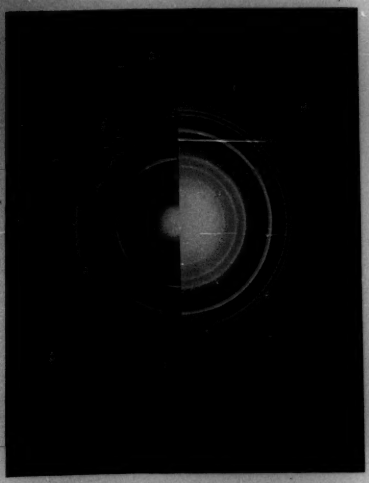

Figure 1. Gold (left) and lithium fluoride (right).

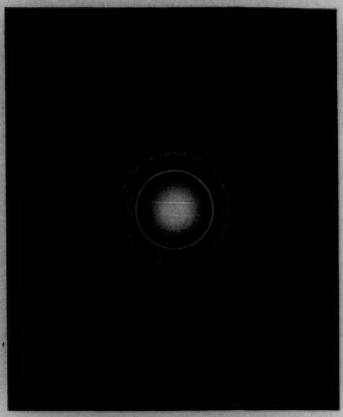

Figure 2. Potassium bromide superimposed on gold.

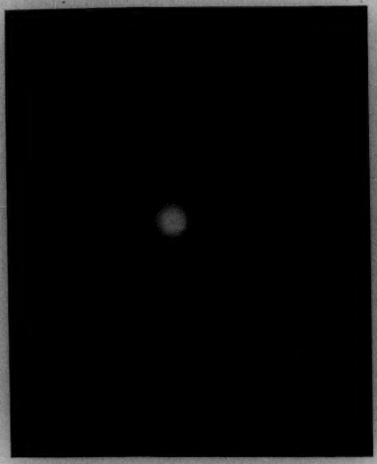

Figure 3. Sodium iodide superimposed on gold.

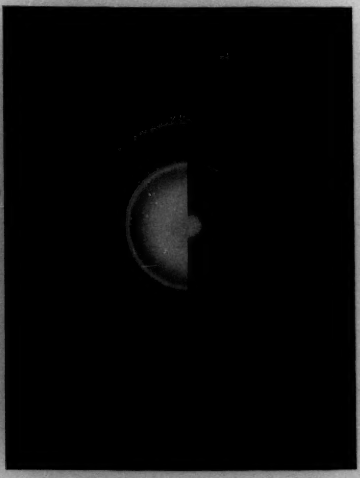

Figure 4. Graphite (left) and gold (right).

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fluorides and chlorides. All the salts were completely soluble in water. The dried graphite contained 0·30 per cent of mineral ash.

The specimens were prepared by flashing in a vacuum of the order of 10^{-6} mm. from an appropriately coated tungsten filament, a procedure which removed any water of crystallization and would tend to reduce the amount of impurities if any were present. The graphite specimens were prepared by the evaporation of a dilute colloidal graphite solution (Aquadag) on a supporting collodion film.

§ 3. THE RESULTS

It will suffice for present purposes to reproduce four typical patterns: figure 1, lithium fluoride double-shuttered with gold; figure 2, potassium bromide superimposed on gold; figure 3, sodium iodide superimposed on gold; and figure 4, graphite double-shuttered with gold. It will be seen that they are such as to lend themselves well to accurate measurement. The results are set forth in the tables, and in order to illustrate the general method of computing the lattice constants, all necessary steps are given in table 1 in the case of the pattern for lithium fluoride double-shuttered with gold, figure 1.

Table 1. Plate F 118. LiF on collodion double-shuttered with gold

Ring-intensity	Ring-diameter (mm.)	Origin	log $2\lambda L$ from gold $a = 4{\cdot}070$ A.	log $2\lambda L$ interpolated	a for LiF (A.)
v.s.	22·245	Au 111	1·7183		
s.	22·485	LiF 111		1·7183	4·025
s.	25·705	Au 200	1·7183		
s.	25·95	LiF 200		1·7183	4·026
s.	36·335	Au 220	1·7184		
s.	36·72	LiF 220		1·7183	4·027
s.	42·605	Au 311	1·7187		
s.	43·03	LiF 311		1·7184	4·030
f.	44·53	Au 222	1·7186		
s.	44·95	LiF 222		1·7184	4·030
f.m.	51·41	Au 400	1·7183		
f.m.	51·985	LiF 400		1·7186	4·029
m.	55·99	Au 331	1·7184		
m.	56·595	LiF 331		1·7186	4·029
m.s.	57·45	Au 420	1·7188		
m.s.	58·125	LiF 420		1·7187	4·025
f.m.	62·985	Au 422	1·7188		
m.s.	63·65	LiF 422		1·7188	4·028
m.s.	66·82	Au 511	1·7187		
f.m.	67·52	LiF 511		1·7188	4·028
f.m.	72·74	Au 440	1·7188		
f.m.	73·545	LiF 440		1·7190	4·027
m.	76·05	Au 531	1·7190		
m.	76·945	LiF 531		1·7190	4·026
m.	77·20	Au 600	1·7189		
m.	78·07	LiF 600		1·7190	4·024
m.	81·34	Au 620	1·7189		
f.m.	82·26	LiF 620		1·7191	4·026
f.	84·44	Au 533	1·7194		
			Mean from fourteen LiF rings		$4{\cdot}027 \begin{matrix}+0{\cdot}003 \\ -0{\cdot}003\end{matrix}$

In column 1 the diffracted intensities are recorded as v.s. very strong, s. strong, m.s. medium strong, m. medium, f.m. faint to medium, and f. faint. The ring diameters were measured between opposite maxima by means of a Cambridge travelling microscope, so arranged as to project a hair-line image onto the photographic plate. log $2\lambda L$ in column 4 was calculated from the equation

$$2\lambda L = \frac{4{\cdot}070D}{\sqrt{(h^2+k^2+l^2)}} \qquad \ldots\ldots(1),$$

λ, L where λ is the wave-length in angstroms, L is the camera-length in millimetres,
, h, k, l D is the diameter of the ring in millimetres, and h, k and l are the Laue indices defining the diffraction.

The values of log $2\lambda L$ in column 5 were obtained by interpolation from those in column 4, whence a for lithium fluoride in column 6 is given by

$$a = \frac{2\lambda L\sqrt{(h^2+k^2+l^2)}}{D}.$$

The advantage of this apparently roundabout procedure is that any deviation from Bragg's law such as might occur, for example, in the event of the refraction of electrons entering and leaving the same crystal-face, would immediately be made evident. The slight increase in the values of log $2\lambda L$ with increasing ring-diameter is due to the fact that equation (1) assumes a spherical recording-field, with a radius of about 48 cm., about the effective specimen, whereas the photographic plate is in fact flat. The complete final results are given in table 2.

In the specification of the crystal-size, "small", "medium" and "large" mean about 40, 60 and 100 A. or more, respectively, but the large crystals were probably submicroscopic as judged by ring-homogeneity. Some specimens yielded sharp continuous rings with superimposed spots; they consisted of large and very large crystals. Since the measurements were made to the homogeneous portions of the rings, however, the effective crystal-size in such cases was large, and has been entered as such in column 6, table 2.

The overall error in the graphite results is, as in the case of all double-shutter patterns, almost certainly due to change in camera-length by amounts of the order of 1 mm. or less, such as is sometimes difficult to avoid on translation of the specimen-carrier between exposures, when the second specimen-half is being brought into the electron beam.

In table 3 are given the means of the lattice constants as set forth in table 2, together with the corresponding X-ray values and the differences between the lattice constants as found by electron-diffraction and X-ray-diffraction respectively. Unless the contrary is stated, the X-ray values are those due to Ewald and Hermann's critical selection in their 1931 supplement to the *Strukturbericht* of the *Zeitschrift für Krystallographie*. As far as we have been able to ascertain, all the X-ray values, including that of gold, are referred to that of sodium chloride ($a = 5{\cdot}6280$ A.) either directly or through secondary standards. Finch and Wilman's[3] electron-diffraction and Bunn's[12] recent X-ray values of the lattice constants of similar samples of coagulated zinc-oxide smoke have also been included in table 3.

Table 2

Substance	Plate No.	Type of pattern	Number of rings other than gold	Mean value of a (A.)	Crystal-size
LiF	F 117	Double-shutter	16	$4{\cdot}028^{+0{\cdot}004}_{-0{\cdot}004}$	Medium
LiF	F 118	Double-shutter	14	$4{\cdot}027^{+0{\cdot}003}_{-0{\cdot}003}$	Medium
LiCl	F 72	Superimposed	7	$5{\cdot}136^{+0{\cdot}003}_{-0{\cdot}003}$	Large
LiBr	F 171	Double-shutter	15	$5{\cdot}500^{+0{\cdot}009}_{-0{\cdot}011}$	Large
LiBr	F 173	Double-shutter	16	$5{\cdot}490^{+0{\cdot}013}_{-0{\cdot}006}$	Large
LiI	F 176	Adjoining specimens	15	$6{\cdot}019^{+0{\cdot}012}_{-0{\cdot}010}$	Medium
NaF	F 53	Superimposed	4	$4{\cdot}641^{+0{\cdot}002}_{-0{\cdot}005}$	Small
NaF	F 170	Double-shutter	7	$4{\cdot}641^{+0{\cdot}009}_{-0{\cdot}006}$	Small
NaCl	F 36	Superimposed	6	$5{\cdot}672^{+0{\cdot}010}_{-0{\cdot}013}$	Medium
NaCl	F 34	Superimposed	9	$5{\cdot}666^{+0{\cdot}010}_{-0{\cdot}014}$	Medium
NaBr	F 52	Superimposed	6	$5{\cdot}966^{+0{\cdot}004}_{-0{\cdot}006}$	Medium
NaBr	F 51	Superimposed	9	$5{\cdot}959^{+0{\cdot}014}_{-0{\cdot}015}$*	Large
NaI	F 69	Superimposed	7	$6{\cdot}468^{+0{\cdot}011}_{-0{\cdot}008}$	Large
NaI	F 68	Superimposed	10	$6{\cdot}469^{+0{\cdot}005}_{-0{\cdot}006}$	Large
KF	B 719	Superimposed	5	$5{\cdot}356^{+0{\cdot}012}_{-0{\cdot}013}$	Small
KCl	F 4	Superimposed	6	$6{\cdot}321^{+0{\cdot}010}_{-0{\cdot}007}$	Medium
KCl	F 6	Superimposed	5	$6{\cdot}317^{+0{\cdot}007}_{-0{\cdot}006}$	Medium
KBr	F 11	Superimposed	11	$6{\cdot}631^{+0{\cdot}008}_{-0{\cdot}010}$	Large
KBr	F 12	Superimposed	11	$6{\cdot}630^{+0{\cdot}004}_{-0{\cdot}005}$	Large
KI	F 17	Superimposed	7	$7{\cdot}078^{+0{\cdot}014}_{-0{\cdot}010}$	Medium
Graphite	F 90	Double-shutter	3	$2{\cdot}462^{+0{\cdot}001}_{-0{\cdot}001}$	Large
Graphite	F 96	Double-shutter	3	$2{\cdot}460^{+0{\cdot}001}_{-0{\cdot}001}$	Large
Graphite	F 99	Double-shutter	3	$2{\cdot}449^{+0{\cdot}001}_{-0{\cdot}003}$	Large
Graphite	F 102	Double-shutter	3	$2{\cdot}459^{+0{\cdot}002}_{-0{\cdot}002}$	Large
Graphite	F 104	Double-shutter	4	$2{\cdot}453^{+0{\cdot}000}_{-0{\cdot}000}$	Large
Graphite	F 107	Double-shutter	4	$2{\cdot}466^{+0{\cdot}001}_{-0{\cdot}002}$	Large
Graphite	F 109	Double-shutter	4	$2{\cdot}456^{+0{\cdot}002}_{-0{\cdot}004}$	Large
Graphite	F 113	Double-shutter	4	$2{\cdot}455^{+0{\cdot}001}_{-0{\cdot}000}$	Large
Graphite	F 114	Double-shutter	3	$2{\cdot}460^{+0{\cdot}003}_{-0{\cdot}003}$	Large

* The width of the error in this case was due in the main to the faintness of the sodium bromide rings in this one pattern.

§ 4. DISCUSSION OF RESULTS

From the results set forth in table 3 it will be seen that the values of the lattice constants of lithium fluoride, chloride and bromide, of sodium bromide and iodide, and of potassium fluoride as determined by electron-diffraction agree within the experimental error with those previously found with X rays though, except in the

Table 3

Substance	Type of pattern	Crystal-size	a (A.) referred by electron-diffraction to the value 4·070 of a_{Au}	a (A.) by X rays	Difference (A.)
LiF	Double-shutter	Medium	4·027 ± 0·005	4·020 ± 0·002	+0·007
LiCl	Superimposed	Large	5·136 ± 0·003	5·143 ± 0·006	−0·007
LiBr	Double-shutter	Large	5·495 ± 0·008	5·489 ± 0·006 [11]	+0·006
LiI	Adjoining specimens	Medium	6·019 ± 0·005	6·000 ± 0·007	+0·019
NaF	Superimposed Double-shutter	Small	4·641 ± 0·004	4·619 ± 0·002	+0·022
NaCl	Superimposed	Medium	5·669 ± 0·005	5·6280	+0·041
NaBr	Superimposed	Large	5·963 ± 0·005	5·962 ± 0·002	+0·001
NaI	Superimposed	Large	6·469 ± 0·005	6·462 ± 0·006	+0·007
KF	Superimposed	Small	5·356 ± 0·010	5·36	?
KCl	Superimposed	Medium	6·319 ± 0·005	6·277 ± 0·002	+0·042
KBr	Superimposed	Large	6·630 ± 0·004	6·586 ± 0·002	+0·044
KI	Superimposed	Medium	7·078 ± 0·008	7·052 ± 0·003	+0·026
Graphite	Double-shutter	Large	2·458 ± 0·005	2·45 ± 0·03 [19]	?
ZnO	Superimposed	Large	$a = 3·258 \pm 0·005$	$a = 3·2426$	+0·015
			$c = 5·239 \pm 0·005$	$c = 5·1948$	+0·044

case of lithium chloride, there is a marked tendency for the electron-diffraction values slightly to exceed those due to X rays. On the other hand, lithium iodide, sodium fluoride and chloride, and potassium chloride, bromide and iodide are like zinc oxide, in giving by electron-diffraction values of the lattice constants higher than those obtained with X rays. The differences in most cases greatly exceed the combined experimental errors due to both methods. In what follows it is our object to elucidate the origin of this discrepancy.

The gold-leaf reference standards employed in these experiments were withdrawn from the same book. The lithium fluoride and bromide, the sodium fluoride and two graphites (F 113 and 114) were compared with the same gold specimen. Of the remaining fourteen gold specimens, seven were compared by the double-shutter method with graphite specimens prepared from the same batch. As is shown in table 2, the individual values of a for graphite agree satisfactorily. In all the graphite specimens the crystals were oriented with the slip planes parallel, or nearly so, to the collodion substrate. The approximate size and shape of colloidal graphite particles have been determined by electron-diffraction by Jenkins [13] and more recently by Finch, Quarrell and Wilman [10]. The fact that beautifully clear and

sharp ring patterns can be obtained by transmission through such graphite films when they are supported on collodion shows that the average particle-size is about 100 A. or less along the *c* axis, but greater in directions normal to that axis; whilst reflection experiments suggest that the particle extent in the planes of the carbon hexagons exceeds 600 A. Thus, bearing in mind the weak attraction between the neighbouring hexagon planes and the very strong C—C bindings within the hexagons, we may reasonably suppose that for the range of particle-size employed in these experiments the value of *a* for graphite is virtually independent of the crystal-size. From the results recorded in tables 2 and 3 we may therefore conclude that, within the present limits of accuracy, the lattice-dimensions of the gold leaf serving as reference standards in these experiments were constant. It should be noted, however, that, owing to the limited accuracy with which *a* for graphite has been determined by X rays, it cannot be assumed that our results prove that the lattice constant obtained for the gold was equal to the X-ray value.

Impurities in the halides examined might affect the values of the lattice constant. Havighurst, Mack and Blake[14] were, however, unable to detect any such effect in the case of ammonium and caesium chlorides containing less than 3 per cent of potassium, caesium or rubidium chlorides, and Vergard and Hauge[15] have shown that the lattice-dimensions of mixed crystals of potassium chloride and bromide vary linearly with composition between the appropriate limits. Thus it seems clear that, in order to give rise to differences of the order of magnitude observed in some of our experiments, gross amounts of impurities would have had to be present in the specimens, whereas analysis showed the materials to be free from all but negligible impurity-contents. Furthermore, in the case of the potassium halides, the tendency of any chemically likely impurity would have been to reduce, but not to increase, the values of the lattice constants.

The halide specimens were supported on either gold or amorphous collodion substrates. Finch and Quarrell[20] have shown that the substrate can exert a profound effect upon the structure, and hence upon the lattice constants of a deposited film. It cannot be supposed, however, that any such pulling into step by the gold substrate of the constituent atoms of the halides occurred in our experiments, because one of the two sodium-fluoride specimens was superimposed on gold and the other on amorphous collodion; nevertheless, both gave results which are in good agreement with each other, though they are higher by 0·4 per cent than the corresponding X-ray value. Furthermore, whilst lithium chloride, and sodium iodide and bromide, all superimposed on gold, gave normal values, similarly mounted specimens of sodium fluoride and chloride, and of potassium chloride, bromide and iodide yielded high electron-diffraction values, in some cases exceeding the corresponding X-ray constant by as much as 0·7 per cent. Finally, although the lithium chloride was deposited on gold but the other lithium halides on collodion, only the iodide gave a high value. Thus these facts seem effectively to negative any explanation of the differences between the electron and X-ray results as being due to a substrate effect.

Thomson[16] has considered the possibility of electrons entering and leaving

through the same crystal faces in polycrystalline specimens. If the crystals were too thick to transmit, this would result in a decrease in ring diameters, relatively large in the case of the inner rings, but decreasing rapidly with increasing angle of refraction, and becoming negligible in the case of the outer rings. As may be seen from table 1, which may be taken as representative of our measurements, we have, however, in no case been able to detect any systematic variation either in log $2\lambda L$ or in the lattice constants deduced from the ring diameters on proceeding outwards from the central spot, other than that due to the flatness of the recording field, an effect which is at least ten times smaller than the refraction effect now under consideration. Again, irrespective of whether the rings are sharp, as in the case of large crystals, or broadened, as in the case of small crystals, the diameters measured between opposite maxima always lead to lattice-constant values which are independent of the ring-diameters. Furthermore, we would expect any pronounced refraction effect to be accompanied by much intense background (zero order) within the innermost ring; apart from the usual halation in the immediate vicinity of the spot, however, the patterns are singularly free from such background. Thus these facts and considerations seem to preclude any possibility of accounting for the abnormally high electron-diffraction values of the lattice constant in terms of refraction by exposed faces.

To sum up. The discrepancies between the X-ray and electron-diffraction values of the lattice constants of certain of the alkali halides enumerated in table 3 cannot reasonably be attributed to (i) a variation in the lattice constant of the gold reference standards, or to (ii) impurities in the halides examined, or to (iii) lattice-distortion through a substrate influence, or to (iv) the coming into play of refractive index effects.

Excessive tolerance in the critical angle of incidence, exceeding, say, 5°, such as has been shown by Finch, Quarrell and Wilman [10] to occur with crystals of extreme thinness in the direction of the beam, would lead not only to a broadening of the rings, but also to an increase in diameter as measured between maxima. Such an effect was not observed and would in any case have led to low electron-diffraction values for the lattice constants.

It is possible from certain features of the patterns to form a very rough estimate of the average size of the halide crystals in the specimens examined. The absence of effects due to excessive tolerance in the angle of incidence suggests a lower limit of particle thickness of roughly 50 A. in the direction of the beam. The freedom from background, particularly inside the innermost rings, places the upper limit of particle thickness as well within 150 A. From the ring definition it can be calculated [17] that the mean overall crystal dimensions in directions normal to the beam varied according to the specimen from about 40 A. to 100 A. or more, and very much more in the case of those crystals which gave rise to spots. In those patterns where spots were obtained, however, they were always superimposed on continuous rings, and since the rings but not the spots served for measurement, the effective crystal-size was of the same order as for those specimens that yielded patterns with perfectly sharp rings without spots. No possible diffraction was found to be missing in any

of the halide patterns. This fact suggests that there was little if any orientation of the crystals. Hence, in view of the cubic symmetry and the clarity of the patterns, it seems reasonable to suppose that the upper limit in the dimensions of the effectively diffracting crystals was less than 150 A. in every direction. Whytelaw-Gray and others [28] found that zinc-oxide smoke on coagulation formed chains of beads about 1000 A. in diameter strung together by links, presumably hairs, so fine as to be invisible through the microscope. The definition and clarity of Finch and Wilman's zinc-oxide patterns are such that the overall dimensions of the effectively diffracting crystals in their specimens must have been not less than 100 A. and not more than 150 A. in the direction of the beam. Thus it seems clear that the zinc-oxide electron-diffraction patterns were due to the invisible hairs, because the size of the beads is such as virtually to preclude their contributing to the diffraction pattern. Conversely, in the case of a similar coagulated zinc-oxide smoke examined with X rays the pattern would be almost entirely produced by the microscopic beads, whose mass must greatly outweigh that of the filamentary links which, with an average diameter of the order of 100 A., would with X rays in any case give rise only to ill-defined haloes. Thus it appears certain that although their zinc-oxide specimens had been prepared in a similar manner and from the same batch of zinc of forensic quality, Finch and Wilman in effect obtained their patterns with crystals of submicroscopic dimensions, whereas those which were effective in producing Bunn's very sharp X-ray powder patterns were at least ten times larger. Similarly, in the case of the halides there is little room for doubt that there existed a similar or even much greater difference in size between the crystals diffracting electrons and X rays respectively.

In the light of these facts and considerations, and in the absence of any other reasonable explanation, it seems to us that the observed differences in the values of the lattice constants of zinc oxide and of certain alkali halides obtained by electron-diffraction and X-ray diffraction respectively are due to a real variation in the lattice-dimensions with crystal-size. In general, the effect is such that the lattice constants appear to be larger for the submicroscopic electron-diffracting crystals than for those of a size effective in yielding sharp X-ray diffractions. Owing to the uncertainty of the X-ray value of a for graphite, however, it is still possible, though perhaps somewhat unlikely, that the value of a for gold having the crystal-size employed by us differs appreciably from the accepted X-ray value of 4·070 A. However this may be, the results set forth above enable the conclusion to be drawn that crystal-size can and sometimes does exert an appreciable effect upon the lattice-dimensions of ionic crystals.

§ 5. ACKNOWLEDGMENTS

We wish to thank Messrs I.C.I. Ltd. and the Research Staff of I.C.I. (Alkali) Ltd. for the precision electron-diffraction camera and the Cambridge Instrument Company for the loan of a travelling microscope.

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536.632:546.321.31

A DETERMINATION OF THE SPECIFIC HEATS OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE

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ABSTRACT. The specific heats of aqueous solutions of potassium chloride have been measured between 15° C. and 45° C., over a range of concentration $\frac{1}{10}N$ to $2{\cdot}5N$. The method of measurement employed was that devised by Ferguson and Miller, slightly modified for use with conducting liquids.

§ 1. INTRODUCTION

In continuation of an investigation of some of the physical properties of solutions of strong electrolytes carried out in this laboratory during the past few years[1,2,3,4], it was considered desirable to study the variation of their specific heats with temperature and concentration. There is quite an extensive literature on the subject, the most valuable work being that of Randall and Rossini[5,6] and of Richards and his collaborators[7]. Much of this, however, did not relate to the direct measurement of specific heat, which was calculated from the heat of dilution. Further, most of the work was carried out at 25° C., and it seemed therefore desirable that observations should be made over a much wider range of temperature.

§ 2. METHOD

The method employed was that described by Ferguson and Miller[8]. Their measurements showed that it was capable of quite high accuracy. Since the publication of their first paper they have made an extensive series of measurements on a number of organic liquids.* They have used a calorimeter of about half the capacity of the original, i.e., about 500 cm.³, while the voltages were measured on a more accurate type of potentiometer reading to 1 μV. It was this apparatus that was used in the present work.

The thermometer which recorded the temperature of the calorimeter and its contents was a first-grade instrument supplied by B. Black and Son, graduated in tenths from $-10°$ to 105° C. With the aid of a low-power microscope readings could be taken to 0·01°. This thermometer was calibrated at the National Physical Laboratory against the standard thermometers, at intervals of ten degrees from 0° to 100°, the limit of accuracy of the test being $\pm 0{\cdot}02°$ C. The calibration was for partial immersion. It is possible to read a temperature on a descending scale, in

* Unpublished.

spite of this being usually regarded as a difficult operation as is evident from the smoothness of the cooling curve.

It will be recalled that electrical power is supplied to the copper calorimeter and its contents to hold the temperature stationary 5°, 10° . . . above that of the surroundings. If E^2/R watts* are supplied and the temperature excess over the surroundings is θ° we have

E, R, θ

$$-\frac{d\theta}{dt}=-(MS+W)\frac{d\theta}{dt}=\frac{E^2}{JR} \qquad \text{.....(1),}$$

where M is the mass of the liquid in the calorimeter, S its specific heat at a temperature θ° above that of the surroundings, W the water equivalent of the calorimeter and its accessories, and $-d\theta/dt$ the rate of loss of heat from the calorimeter and its contents at temperature-excess θ°.

M, S W t

It is found empirically that

K

$$-\frac{d\theta}{dt}=K\theta^{\frac{5}{4}} \qquad \text{.....(2).}$$

The validity of this equation may be established as follows. Integrating (2), we have

$$\theta^{-\frac{1}{4}}-\theta_0^{-\frac{1}{4}}=\tfrac{1}{4}Kt \qquad \text{.....(3).}$$

A series of values of θ and t are obtained from a cooling experiment, so that if we plot $\theta^{-\frac{1}{4}}$ against t we should obtain a straight line, the slope of which determines K, if equation (2) holds. K is a constant for a given solution and calorimeter, but varies slightly from solution to solution. It is separately determined for each run. We thus obtain the equation

$$(MS+W)\,K\theta^{\frac{5}{4}}=E^2/RJ \qquad \text{.....(4),}$$

for the determination of S.

The water equivalent is determined by making a complete run with water as the experimental liquid, and substituting values taken from the International Critical Tables for the specific heat of water. This gives the relation

$$W_T=W_0\,(1+0{\cdot}0005009\,T)$$

T for the variation of the water equivalent with temperature, where T is in degrees centigrade.

§ 3. MODIFICATION OF CALORIMETER FOR CONDUCTING LIQUIDS

It was obvious that for conducting liquids such as electrolytes it would be necessary to insulate the heating-coil and leads. A very thin coat of cellulose lacquer was applied to the coil, leads, and inner wall of the calorimeter, but a run with a normal solution of potassium chloride soon revealed the necessity for better insulation and for keeping the solution from contact with copper. The calorimeter was therefore chromium-plated.

* International watts, the appropriate value of J being 4·1845. If we follow the recommendation in the S.U.N. report of the International Conference on Physics, that the unit of heat when measured in units of energy be the force defined as 10^7 ergs, the value of J is $4{\cdot}18_8$. This change involves an alteration of about 0·05 per cent in the values of specific heats given in this paper.

After a number of methods of insulating the coil had been tried, that finally used was to apply a thin coat of Bakelite varnish which was baked on.

Apart from these minor though necessary alterations, Ferguson and Miller's procedure was adhered to throughout.

§ 4. RESULTS

All measurements were made with accurately prepared solutions, the water being obtained from a conductivity still. The salts were of analytical-reagent standard. As soon as the solution had been prepared it was put into the calorimeter and a complete run was carried out. The solutions were never allowed to stand in the calorimeter for more than two days. As a rule the whole experiment was completed within six or seven hours.

The results of the measurements on solutions of concentrations ranging from $\frac{1}{10}N$ to $2{\cdot}5N$ are collected in tables 1 and 2. In this work a normal solution is defined as one containing 1 gram-molecule (74·553 g.) of potassium chloride in 1000 g. of water. When the results are plotted it is found that the temperature coefficient decreases with concentration, until with a $\frac{1}{2}N$ solution it is zero within the limits of experimental error. Below this concentration an approximately parabolic curve is obtained when specific heat is plotted against temperature, as in the case of water.*

Table 1

(*a*) Heating experiments. Normal solution of potassium chloride. Mass of liquid, 495·45 g.

E (V.)	Temperature of surroundings	Temperature of calorimeter	Temperature excess	Water equivalent W	Specific heat
$0{\cdot}1841_5$	13·34	15·21	1·87	66·47	$0{\cdot}911_4$
$0{\cdot}4111_9$	13·34	18·96	5·62	66·64	$0{\cdot}912_0$
$0{\cdot}5704_0$	13·35	24·75	11·40	66·83	$0{\cdot}912_5$
$0{\cdot}7180_9$	13·36	29·82	16·46	67·08	$0{\cdot}913_6$
$0{\cdot}9118_2$	13·36	37·44	24·08	67·38	$0{\cdot}915_1$
$1{\cdot}0136_8$	13·37	41·87	28·50	67·48	$0{\cdot}916_3$

(*b*) Cooling experiments. $K=0{\cdot}06972\times10^{-3}$.

Temperature of calorimeter	Temperature of surroundings	Time t (sec.)	Temperature of calorimeter	Temperature of surroundings	Time t (sec.)
31·32	13·34	0	26·33	13·36	2400
30·59	13·35	300	25·32	13·35	3000
29·88	13·36	600	24·46	13·35	3600
28·59	13·37	1200	23·62	13·35	4200
27·29	13·37	1860	18·50	13·33	10200

While the accuracy of the work is quite reasonably high, it is not however sufficiently great for us to calculate some of the associated thermodynamic functions

* Work on the specific heat of water is now in progress.

Table 2. Potassium chloride

2·5N	T(° C.)	15·61	19·14	23·32	25·79	31·66	37·20	40·53	
	S	$0{\cdot}813_8$	$0{\cdot}814_7$	$0{\cdot}816_9$	$0{\cdot}817_7$	$0{\cdot}820_1$	$0{\cdot}822_3$	$0{\cdot}824_2$	
2N	T(° C.)	14·72	17·96	21·13	26·22	30·47	33·81	36·65	40·04
	S	$0{\cdot}839_0$	$0{\cdot}840_5$	$0{\cdot}842_2$	$0{\cdot}843_7$	$0{\cdot}845_2$	$0{\cdot}846_0$	$0{\cdot}847_1$	$0{\cdot}849_6$
1·5N	T(° C.)	14·94	18·95	24·96	28·57	32·90	38·24	45·06	
	S	$0{\cdot}872_2$	$0{\cdot}873_5$	$0{\cdot}875_0$	$0{\cdot}875_5$	$0{\cdot}876_5$	$0{\cdot}877_3$	$0{\cdot}879_4$	
0·75N	T(° C.)	22·61	28·97	34·48	40·85	44·41	50·64		
	S	$0{\cdot}931_8$	$0{\cdot}932_4$	$0{\cdot}933_3$	$0{\cdot}934_1$	$0{\cdot}934_2$	$0{\cdot}935_0$		
0·5N	T(° C.)	16·11	20·95	26·76	31·48	33·90	38·42	42·78	
	S	$0{\cdot}955_6$	$0{\cdot}955_2$	$0{\cdot}955_6$	$0{\cdot}955_8$	$0{\cdot}955_4$	$0{\cdot}955_7$	$0{\cdot}955_8$	
0·5N	T(° C.)	16·27	22·25	29·81	36·34	42·63			
	S	$0{\cdot}956_0$	$0{\cdot}955_7$	$0{\cdot}955_8$	$0{\cdot}955_4$	$0{\cdot}956_1$			
0·1N	T(° C.)	16·37	19·30	23·86	29·11	33·73	38·82	43·15	
	S	$0{\cdot}988_5$	$0{\cdot}987_1$	$0{\cdot}987_2$	$0{\cdot}987_1$	$0{\cdot}987_5$	$0{\cdot}987_9$	$0{\cdot}988_2$	

such as the apparent partial molal heat-capacity of the electrolyte. It is not therefore possible to test the agreement of the present data with the Debye theory which predicts that the partial molal heat-capacity should vary linearly with the square root of the concentration. For such calculations to be made an accuracy of about 1 part in 10,000 is required.

Randall and Rossini have derived the expression

$$C_p = 2{\cdot}14\,(\Sigma\nu_1 z_1^2)^{\frac{5}{2}}\, m^{\frac{1}{2}} + C_{p_0} \qquad \text{.....(5),}$$

C_p, m where C_p is the partial molal heat-capacity, and m the molarity, while $\Sigma\nu_1 z_1^2$ is the valence factor. C_{p_0} is the value of the partial molal heat-capacity at infinite dilution. Later work may permit of a strict test of the above relation over a temperature-range, its validity at 25° C. having been proved for a number of electrolytes of different types[5].

Theory does not predict any simple relation between specific heat and concentration, nor do the experimental data suggest one. The equation connecting the specific heat and the partial molal heat,

$$C_p = S\left[\frac{1000}{m} + M\right] - \frac{1000}{m} \qquad \text{.....(6),}$$

taken in conjunction with the theoretical relationship between C_p and the concentration, equation (5), shows immediately that the specific heat is a complex function of the molarity.

§ 5. CONCLUSIONS

The present preliminary note is designed to show the possibility of determining the specific heats of solutions of electrolytes and their variation with temperature over a relatively wide range of temperature with a fairly high degree of accuracy. In

a later communication it is hoped to extend these results in range and in accuracy, and to discuss their theoretical bearing.

§ 6. ACKNOWLEDGMENTS

I have much pleasure in expressing my thanks to Prof. H. R. Robinson, F.R.S., and to Dr Allan Ferguson for the facilities they have placed at my disposal and for their advice and encouragement. I am indebted to the Department of Scientific and Industrial Research for a grant which made it possible to carry out this work.

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THE CONDUCTIVITY OF AN ORIFICE IN THE END OF A PIPE

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ABSTRACT. The conductivity of an orifice in an infinite plane of negligible thickness was shown by the late Lord Rayleigh to be equal to its diameter d. The writer extended this formula to include the conductivity when one side of the plane is enclosed by a concentric pipe of diameter D, which thus forms a cylindrical resonator fitted with an infinite plane at the mouth, and deduced the expression $d.2^{d/D}$ for the conductivity. This expression is supported by experimental results quoted in the present paper.

THE resistance experienced by an alternating current of fluid entering a semi-infinite atmosphere of the fluid from an orifice in an infinite plane is equal to[1] $1/4kr$, where k stands for the conductance of the medium and r for the radius of the orifice.* This formula also holds if the current enters the orifice from the semi-infinite atmosphere, hence the resistance encountered by the alternating current in passing into a semi-infinite atmosphere from a similar atmosphere through an extremely thin orifice is given by

k, r

$$1/2kr.$$

By putting k equal to 1, we make the conductivity of the orifice $2r$, which is equal to the diameter and is the well-known value for the acoustical conductivity for such an orifice[2].

If, however, the efflux takes place through a pipe of radius r terminating in an infinite flange, the resistance *due to the orifice* is $1/4kr$, and therefore the conductivity of the latter is $2d$, where d is the diameter.

d

If the pipe is of larger radius than the orifice, the conductivity will lie between d and $2d$. The writer has shown[3] that the expression

$$C = d.2^{d/D},$$

closely represents the conductivity C of an orifice of diameter d in the end of a pipe of diameter D, fitted with an infinite flange.

C

N. W. Robinson[4] used this formula for calculating the conductivities of orifices

* The resistance $1/4kr$ is only true for direct current, but is very near the truth for a.c. of low frequency. Rayleigh made this assumption in developing the theory of resonators, see *Sound*, p. 170.

for comparison with results obtained by him experimentally and shown in the table.

Table

Diameter d of orifice (cm.)		4·0	3·5	3·0	2·5	2·0	1·5	1·0
Mean of conductivities at 875 to 1120 c./sec.	Experimental	8·38	6·67	5·30	4·05	3·04	2·08	1·28
	Calculated	7·02	5·73	4·58	3·56	2·65	1·86	1·15
Reduced conductivity at 875 c./sec.		6·9	5·72*	4·62	3·54	2·49	1·79	1·10

* The actual figure given for the 3·5-cm. orifice is 5·53, but, from the run of the table, it appears that this should be 5·23. This reduces, for a thin plate, to 5·72, the value given above.

Unfortunately, in these experiments it was necessary for the diameter of the pipe, which was about 5 cm., to be small in comparison with the wave-length of the sound used. Robinson used frequencies of 875, 912, 1000 and 1120 c./sec., and his results show a considerable increase of conductivity with frequency in practically every case.

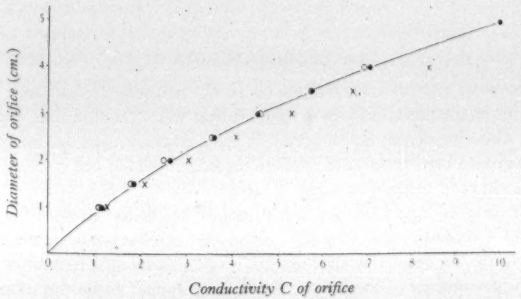

Figure 1. ● Formula, $C=d.2^{d/D}$; × Robinson, experimental; ○ Robinson, reduced results.

The experimental results given above are the mean values for the four frequencies, whereas the values for the lowest frequency, quoted in table 3 of Robinson's paper[4] have, when reduced so as to be applicable to a thin plate, the values shown in the last line of the accompanying table.

It will be seen from the graph that these are practically the same as the calculated values, and therefore confirm the formula.

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THE ABSOLUTE MEASUREMENT OF THE VISCOSITY OF LIQUID TIN

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ABSTRACT. By the capillary-flow method the viscosity of liquid tin has been measured over a range of temperature just above the melting-point. The kinetic-energy correction has been determined independently by the use of Knibbs's graphical method. The viscosity values are in good agreement with the measurements of Stott, and confirm the general accuracy of the work of Sauerwald and Töpler. The temperature variation of the viscosity and the value at the freezing-point can be adequately represented by Andrade's theory of the viscosity of liquids.

§ 1. INTRODUCTION

In the course of a series of investigations on the temperature variation of certain properties of the metal tin it was realized that more reliable data were needed for the viscosity of the liquid metal at temperatures near the melting-point. This paper gives a brief account of detailed measurements of the viscosity of liquid tin over the range of temperature 235° C. to 330° C.

The viscosity of liquid tin and other metals has been measured by Arpi[1], Plüss[2], and Sauerwald and Töpler[3], using the capillary-flow method, and by Fawsitt[4], using the oscillating disc method. The results obtained differ considerably; the measurements of Sauerwald and Töpler appear to be the most accurate of those mentioned.

Recently measurements on the viscosity of liquid tin have been made by Stott[5] by the use of an oscillating disc. By using the results of Sauerwald and Töpler for calibration purposes, Stott has extended the range of temperature for which the viscosity may be taken as fairly well established, but has pointed out the desirability of checking the measurements of Sauerwald and Töpler.

§ 2. METHOD

After a close examination of the available methods, the capillary-flow method was chosen since it appeared most capable of providing absolute values; all oscillatory methods were rejected owing to the theoretical uncertainties which they involve.

$\frac{t}{V}$ The capillary-flow method is that in which the time t taken by a known volume V of the liquid to flow through a vertical capillary tube under a known pressure-

difference P is measured. If r is the radius of the capillary and l its length, the viscosity η is given by the simple Poiseuille relation P, r, l η

$$\eta = \frac{\pi P t r^4}{8Vl},$$

all corrections being ignored.

§ 3. THEORETICAL CORRECTIONS

The kinetic-energy correction. The simple Poiseuille law is derived on the assumption that all the energy supplied during flow is used in overcoming viscous resistance within the fluid. If moderate or high speeds are used, a correction for the gain in kinetic energy is necessary. The final formula for the viscosity with this correction was first given by Hagenbach as

$$\eta = \frac{\pi P t r^4}{8Vl} - \frac{mV\rho}{8\pi lt} \qquad \text{.....(1),}$$

where m is a constant and ρ is the density of the liquid. m, ρ

Various theoretical values of the constant m, ranging from 1·00 to 1·12, have been proposed from time to time. In practice, however, there is evidence that m is not strictly the same for all tubes and that it may even vary slightly for a single tube. The kinetic-energy correction is of especial importance in the case of liquid metals, since the density is a multiplying factor in the correction term.

Knibbs's method[6]. Fortunately Knibbs's experimental procedure provides a valuable method of estimating whether or not m is constant for a particular tube, and for independently estimating its magnitude. Equation (2) can be re-written

$$Pt = a + \frac{b}{t},$$

where $$a = \frac{8\eta Vl}{r^4\pi} \text{ and } b = \frac{m\rho V^2}{\pi^2 r^4}.$$ a, b

If Pt is plotted against $1/t$ for a given tube and liquid, we get a straight line whose slope enables m to be calculated. If a close fit is obtained, it may be assumed that m is constant for the tube.

This method has been applied successfully to many viscosity-measurements, but apparently no attempt has been made in the case of a liquid metal, although in the latter case the effect of the correction is much more pronounced. The application of this procedure in the present work has been entirely successful.

The mean pressure head of the metal in the capillary. In calculating the pressure effective in producing flow through the capillary for the case in which the liquid is forced upwards through the capillary, the mean pressure head of the liquid metal must be subtracted from the applied manometric pressure. In general it is not sufficiently accurate to deduct from the applied pressure the arithmetic mean of the initial and final hydrostatic heads, especially when low velocities are used. In these

experiments the tube containing the volume V was of constant circular section, so that simple integration gives for the effective pressure

$$P=(h_2-h_1)\,\rho g \Big/ \log_e \frac{H-h_1}{H-h_2} \qquad \text{.....(2),}$$

H, h_1, h_2 where H is the applied pressure head and h_1 and h_2 are the initial and final hydrostatic heads of the metal in the capillary, all in centimetres of metal. This formula of course ignores the effect which the kinetic-energy correction has on the value of effective pressure.

The corresponding formula including this correction[7] is

$$\frac{P}{\rho g}=H_1+\tfrac{1}{4}KH_1^2 \qquad \text{.....(3),}$$

H_1 where $$H_1=\frac{h_2-h_1}{x_1-x_2+\log_e(x_1/x_2)},$$

x_1 $$x_1=\sqrt{\{1+K(H-h_1)\}}-1,$$

x_2 $$x_2=\sqrt{\{1+K(H-h_2)\}}-1,$$

K and $$K=\frac{mg\rho^2r^4}{16\eta^2l^2}.$$

A comparison of the two formulae by a series of calculations shows that if K is sufficiently small the error introduced by the use of formula (2) can be ignored over a wide range of applied pressures. Taking h_1 and h_2 as approximately equal to 5·5 and 8·5 cm. respectively, the percentage difference between formulae (2) and (3) is negligibly small down to an applied pressure of about 9·0 cm., if K is less than 0·5. With the tubes employed in this work, for which K ranged from 0·18 to 0·33 for mercury, and from 0·02 to 0·04 for tin, the use of formula (2) gave sufficiently accurate values throughout.

The end correction. Allowance was made for the end effect by repeating the observations with the viscometer tube shortened by a known amount. The ratio of length to diameter was about 200, and the correction amounted to approximately 0·5 per cent.

§ 4. DESCRIPTION OF THE APPARATUS

Figure 1 shows the principal parts of the apparatus used.

Capillary apparatus. The capillary tube *ab* was 10 cm. long, with internal diameter about 0·05 cm. It opened into a wider cylindrical tube *E*, 10 cm. long with internal diameter 2·5 cm. The join between the capillary and its extension was such that the bore did not end abruptly, but was slightly funnel-shaped to facilitate linear flow.

Oxidation of the liquid metal was one of the most important difficulties to be met, since traces of surface impurity block the capillary and cause considerable variations in results. Oxidation was reduced by circulating hydrogen through the viscometer and by using a carbon vessel *C* as container for the tin. This container was supported on a spiral spring *S* to lessen the risk of breakage of the tube on expansion and contraction. The viscometers used were of Vitreosil transparent quartz.

The time of flow had to be recorded electrically and was determined by the use of platinum contacts Y_1 and Y_2 which defined the measured volume; the contacts and a wire dipping into the metal were connected to an electric timing circuit. The contacts were sealed into the ends of narrow conducting tubes.

The viscometer was fitted into the outer cylinder D, made of brass, by means of a heat-resisting ring, and the whole apparatus made gas-tight with a high-temperature cement.

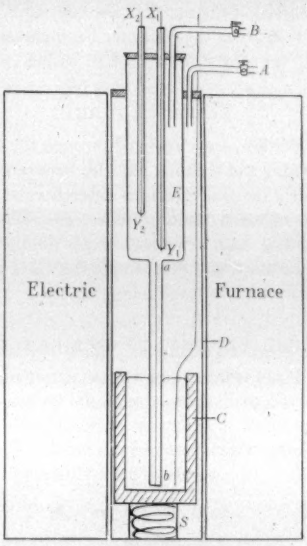

Figure 1. Capillary apparatus.

Pressure arrangement. On account of drainage and surface tension it was necessary to measure the time taken for the metal to fill the volume V rather than the time taken to empty it. The pressure-difference was usually obtained by sending hydrogen under pressure through tap A into the outer vessel. The hydrogen was subjected to this excess pressure by the use of a constant-pressure head device, which could itself be varied. In test experiments with mercury, however, where excess pressures up to 20 cm. of mercury were required, it was convenient to obtain part by reducing the pressure inside the capillary instead of applying the whole pressure to the outer vessel. For this purpose a water pump could be connected to the tap B through a 3-way tap. By using an additional 3-way tap it was possible to send hydrogen through the apparatus in both directions, and to apply excess or reduced pressure both inside and outside the capillary as required. By this means the possibility of the formation of surface oxide was considerably

reduced, and the movement of the liquid metal in the viscometer could be controlled more readily after each measurement. Two manometers were used differentially—a mercury manometer for pressures greater than 10 cm. of mercury, and a water manometer for smaller pressures.

Temperature-control and measurement. The apparatus was heated in an electric furnace 30 cm. long. Temperatures were measured by thermocouples of chromel-alumel, in conjunction with a precision potentiometer. One thermocouple was placed just above the surface of the metal in the container, and another as near as possible to the volume V between the contacts. Temperatures could be maintained constant to within $\frac{1}{2}$° C. for 2 or 3 hours, and to within $\frac{1}{10}$° C. for short periods.

§ 5. PROCEDURE

In all experiments hydrogen was circulated through the sealed apparatus during the whole process of heating and melting, and also between observations. The time of flow was recorded for a range of pressure-differences at each temperature, and each measurement was repeated three or four times. The hydrostatic heads h_1 and h_2 were determined at each temperature by noting the applied pressures necessary just to start the clock and just to stop the clock respectively. ht, where $h = P/\rho g$, was plotted against $1/t$ for each temperature.

§ 6. MEASUREMENTS ON MERCURY

The apparatus was tested with mercury in order to determine the accuracy for absolute measurements. Figure 2 shows the results for the two tubes used. It can

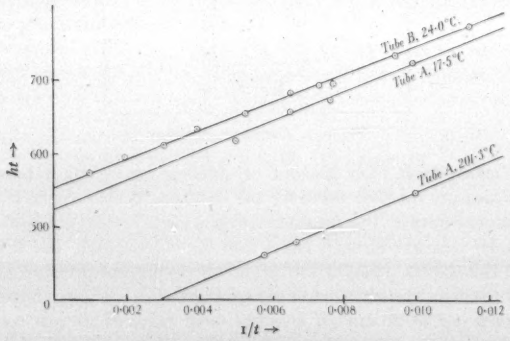

Figure 2. Results for mercury.

be seen that the points lie close to a straight line in each case, and consequently the magnitude of the kinetic-energy correction could be determined from the experiments.

The value of m obtained from figure 2 was 1·01 for tube A and 1·12 for tube B.

The values of the viscosity calculated from equation (1) for tube *A* are $0{\cdot}0158_2$ poise at 17·5° C. and $0{\cdot}0099_4$ poise at 200° C. Measurements with tube *B* were made at one temperature only and gave a mean value for η of $0{\cdot}0153_8$ poise at 24° C.; the results for this tube are shown in table 1.

Table 1. Results for mercury at 24° C. Tube *B*; radius 0·02549 cm.

Applied pressure (cm. of mercury)	Effective pressure (cm. of mercury)	Time (sec.)	Kinetic-energy correction	Viscosity (poises)
8·46	1·18	502·5	0·00103	0·01541
9·07	1·95	314·4	0·00164	0·01535
10·52	3·52	185·2	0·00279	0·01528
11·49	4·52	150·9	0·00342	0·01548
13·93	6·98	104·9	0·00492	0·01538
			Mean	$0{\cdot}0153_8$

The fact that the graphical method yielded a series of straight lines showed that, although the kinetic-energy correction was appreciable, the use of formula (2) for the effective pressures gave sufficiently accurate viscosity values.

§ 7. MEASUREMENTS ON TIN; COMPARISON WITH OTHER AUTHORS

In view of the satisfactory results for mercury a comprehensive series of observations was made with tin over a range of temperature 235° C. to 330° C. The results are shown in figures 3 and 4. The points marked by crosses in figure 3 relate to measurements in which very inconsistent values of the time of flow were obtained. With tube *B*, individual time-measurements usually agreed to 1 part in 150 and showed that there was apparently little oxidation.

Table 2. Typical results for tin at 271° C. Tube *B*

Applied pressure (cm. of tin)	Effective pressure (cm. of tin)	Time (sec.)	Kinetic-energy correction	Viscosity (poises)
10·59	2·34	626·1	0·00047	0·01785
12·32	4·23	350·6	0·00085	0·01770
14·10	6·06	250·2	0·00118	0·01778
15·38	7·37	208·5	0·00142	0·01780
16·57	8·59	180·3	0·00164	0·01770
17·76	10·09	155·2	0·00191	0·01767
			Mean	$0{\cdot}0177_5$

Table 2 shows a typical set of results at a particular temperature; between 400 and 500 measurements were made in all. The effective pressures usually varied between about 2 cm. and 10 cm. of tin, and the time of flow ranged accordingly from 700 sec. to 120 sec. approximately. Plüss's smoothed values for the density of liquid tin were used; these are about 0·3 per cent higher than the figures used by

Sauerwald and Töpler. The accuracy obtained for the viscosity numbers is about 0·7 per cent.

Table 3 shows the variation of the viscosity of liquid tin with temperature; these mean values are taken from figure 5, which shows the comparison with the results obtained by Plüss, Sauerwald and Töpler, and Stott. The end correction is made only for the measurements with tube *B*, since tube *A* was broken early in the course of the work. The effects of expansion were negligibly small except for a small correction for the increase in length of the capillary tube.

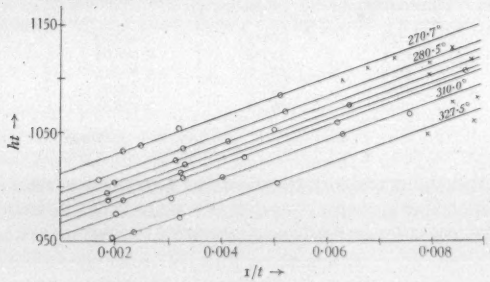

Figure 3. Results for tin, tube *A*.

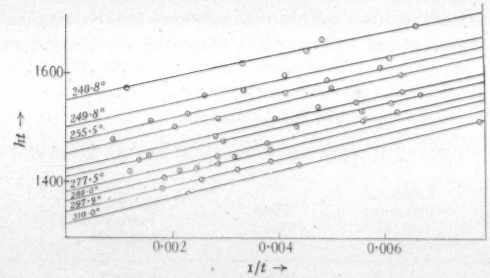

Figure 4. Results for tin, tube *B*.

Over the common range these results are from 3 to 7 per cent higher than those of Plüss. The curve cuts that of Sauerwald and Töpler a little above 300° C.; above this temperature, over the common range, the numbers are from 0 to 3 per cent higher, and below it they are from 0 to 1 per cent lower. The best agreement is with Stott's numbers, obtained with an oscillating disc; up to 300° C. the mean difference is less than 1 per cent. This agreement is all the more interesting in view of the fact that Stott's results are to a certain extent based on Sauerwald and Töpler's smoothed values. Undoubtedly the last-named authors' work was of great precision and it is difficult to find any source of systematic error in it. The

Table 3. Viscosity of liquid tin

Temperature (° C.)	Density (g./cm³)	Viscosity (poise)
235	6·967	0·0195
240	6·963	0·0192
250	6·958	0·0186
260	6·952	0·0181
270	6·946	0·0176
280	6·941	0·0173
290	6·934	0·0170
300	6·927	0·0167
310	6·920	0·0164
320	6·914	0·0162
330	6·909	0·0160

exact shape of their curve, however, below 300° C. is difficult to ascertain, and it seems probable that the agreement of the present results with those of Stott is an indication of the general accuracy of Sauerwald and Töpler's measurements.

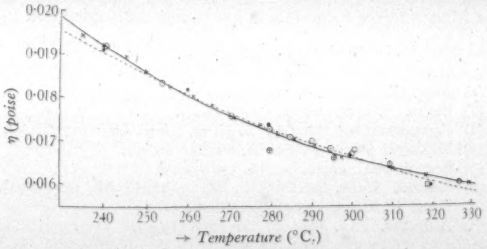

Figure 5. Stott: ●; broken curve. Sauerwald and Töpler: ⊡. Plüss: ⊕. Author: ⊙ tube *A*, × tube *B*, full curve.

§ 8. THE TEMPERATURE VARIATION OF VISCOSITY, AND THE VISCOSITY AT THE FREEZING-POINT

The temperature variation of the viscosity values shown in table 2 can be adequately expressed by the equation recently proposed by Andrade[8]:

$$\eta v^{\frac{1}{3}} = Ae^{c/Tv},$$

where v is the specific volume, T is the absolute temperature, and A and c are arbitrary constants. This equation fits the experimental data very closely for a large number of organic liquids, and has been applied successfully in the case of

mercury. The greatest percentage difference between the experimental results for tin and the values calculated from the equation is $-1{\cdot}0$ per cent, whilst the mean difference is $0{\cdot}1$ per cent. The agreement is very satisfactory since it is of the same order as the limit of experimental error.

The viscosity of liquid tin at the freezing-point, deduced from these experiments, is $0{\cdot}0197$ poise, as compared with Stott's value of $0{\cdot}0195$ poise, and Sauerwald and Töpler's extrapolated value of $0{\cdot}020$ poise. All these numbers are in good agreement with the value $0{\cdot}019$ poise calculated for tin according to Andrade's theory of the viscosity of liquids.

§ 9. CONCLUSION

The experiments show that the kinetic-energy correction can be determined experimentally, and consequently that absolute measurements of the viscosity can be made. The results indicate the general accuracy of the measurements made by Sauerwald and Töpler. Their data can therefore be used for calibration purposes in Stott's procedure for liquid metals, for which the flow method is not easily applicable.

§ 10. ACKNOWLEDGMENTS

The author is pleased to express his thanks to Prof. H. R. Robinson for his encouragement during the course of this work, undertaken in the physical laboratories of Queen Mary College; to Dr J. P. Andrews for his interest and suggestions throughout; and finally, to the Department of Scientific and Industrial Research and to Queen Mary College for grants in connexion with the work.

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DISCUSSION

Dr Bruce Chalmers. Comparatively small quantities of impurity are known to have a disproportionately large influence on some of the physical properties of metals. In particular, impurities that change the melting-point would be expected to affect the viscosity just above that point. It would increase the value of the paper if the author could give an analysis of the tin after use, that is, after it had taken up any free metal that may have been present in the carbon vessel.

Author's reply. Various samples of tin were used in the measurements and in no case was the purity less than $99{\cdot}5$ per cent. Unfortunately no quantitative analysis of the impurities was made either before or after use.

621.396.674

ON THE CURRENT-DISTRIBUTION IN A LOOP AERIAL

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Communicated by Prof. L. S. Palmer, July 9, 1935, and in revised form August 16, 1935. Read in title November 15, 1935

ABSTRACT. The work described in this communication is a continuation of a previous investigation on the current-distribution round a short-wave frame aerial. The present development deals with the determination of an expression for the amplitude of the current at any point in the aerial, and the resulting theoretical conclusions are tested by using a circular loop aerial of perimeter 11·3 m. The effect of damping is considered, and the probable value of the attenuation constant is calculated.

§ 1. INTRODUCTION

In a recent investigation[1] into the properties of loop aerials when used with short waves, it was found desirable to have some information concerning the distribution of current. This is especially necessary when the ratio of the dimensions of the loop to the wave-length is of the order of unity because under these conditions the current varies greatly from point to point in the loop. Further, the non-uniformity of the current affects the radiation characteristics and hence, in order to obtain a proper understanding of the action of an aerial of this kind, it is desirable to know the exact current distribution and how this distribution is modified as the wave-length changes. It is for these reasons that the following work was undertaken.

§ 2. PREVIOUS WORK

A preliminary account of the work has already been given in a previous communication[2]. It was shown in that paper that when an incident wave or local oscillator actuates a loop aerial at a given point P, figure 1, the electric force causes a charge at P to oscillate to and fro at the frequency of the wave. The resulting disturbance travels round the loop with approximately the velocity of the wave in the surrounding medium and, by considering the disturbance propagated round and round the loop an infinite number of times in both directions, an expression was obtained giving the position and magnitude of the current antinodes.

It was deduced from the theory that (i) all the current antinodes are at a fixed distance from P, which is a fixed point determined by the position of the initial oscillation; (ii) the distribution of the nodes and antinodes round the loop is fixed in space, and in the case of a loop used as a receiver it is independent of the orientation

of the loop to the wave-front; (iii) the disposition of the current antinodes is symmetrical about the line PP', figure 1; (iv) current antinodes always occur at P' irrespective of the wave-length; (v) successive current antinodes are $\frac{1}{2}n\lambda$, where n is an integer and λ is the wave-length, from P' measured in both directions round the loop.

n
λ

In the previous paper a number of preliminary experiments which confirmed these results were described. It is the object of the present work to describe the

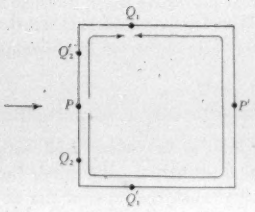

Figure 1.

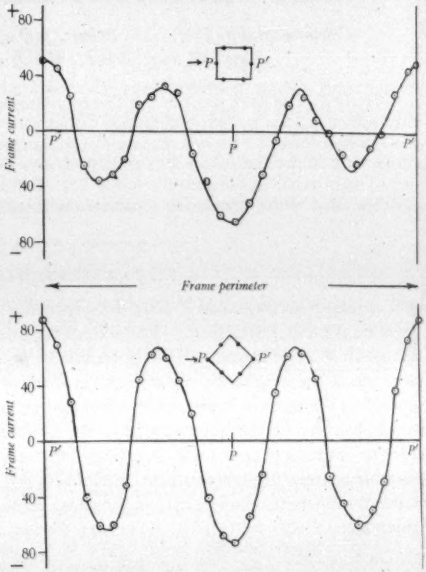

Figure 2. The current-distribution in the square and diamond positions. $\lambda = 3{\cdot}74$ m., $l = 12{\cdot}44$ m.

results of more detailed experiments, and to extend the theory so as to facilitate the experimental verification of certain deductions concerning the magnitude of the amplitude variations.

The preliminary experiments were carried out with a square frame and the current was measured with a thermojunction inserted in the frame wire. Figure 2 gives the results of some measurements made with a square frame of perimeter 12·44 m. on a wave-length of 3·74 m. The upper graph gives the current-distribution when the frame is oriented in the square position, i.e. with the wave-front parallel to one side of the frame, whilst the lower graph gives the current-distribution when the frame is oriented in the diamond position, i.e. with the

wave-front at 45° to the side of the frame. In each case the results are, within the limits of experimental error, in accordance with the deductions from the theory, but it is also apparent that although the waves remain fixed in space the current-distributions in the two cases are not exactly the same. This is because the actual current at any point of a rectangular frame depends not only on the initial effect arising from the circulation of electric waves round the frame-perimeter, but also on a supplementary effect due to reradiation between the parallel wires of the frame. In the case of a frame used for reception, this radiation effect is dependent on the orientation of the frame to the wave-front, and consequently the supplemental current due to this radiation may augment[3] the initial current to different extents in the two cases, and so modify the current-distributions as shown in figure 2. To obviate this supplementary effect between the parallel limbs of a rectangular frame, it was decided that a circular loop aerial should be used in the present experiments, because with such a loop there are no parallel wires which can give rise to the disturbing radiation effects referred to above.

§ 3. THEORETICAL CONSIDERATIONS

In the theory given previously an expression giving the magnitude of the current antinodes was developed. The problem will now be considered from a different point of view and an expression will be calculated for the magnitude of the current at any point in the loop.

Consider a pair of transmission lines of length $\frac{1}{2}l$ connected to a generator at one end and short-circuited at the other. If the primary constants of the line are R, L, C and G per unit length, then it can be shown[4] that

l

$R, L, C,$

$$I_g = \frac{V_g}{Z_0} \coth \tfrac{1}{2} Pl \qquad \text{.....(1),}$$

where I_g and V_g represent the current and voltage in the line as measured at the generator, Z_0 is the (complex) characteristic impedance, and $P = \alpha + j\beta$, where α is the attenuation constant, β is the wave-length constant and j is $\sqrt{(-1)}$.

I_g, V_g

Z_0, P, α

β, j

It follows from equation (1) that the current at a point in the line at a distance x from the generator is given by

x

$$I_x = \frac{V_g}{Z_0} \operatorname{cosech} \tfrac{1}{2} Pl \cosh P(\tfrac{1}{2}l - x) \qquad \text{.....(2).}$$

This equation can be used for calculating the amplitude of the current at any point in the loop.

In the analysis given above the e.m.f. induced at the point P has alone been considered, whilst in actual fact a second e.m.f. induced at the point P' might have been expected. However, the experimental results of the previous papers show that this second e.m.f. is of negligible importance in determining the current-distribution. This may be seen by referring to figure 6 of the paper by Palmer, Taylor and Witty[2] and figure 3 of the paper by Palmer and Witty[3]. In both these cases if the effect of the e.m.f. induced at P' had been appreciable, then additional current

antinodes, symmetrically placed with respect to those actually observed, would have been present.

Equation (2) will now be used to determine the variation of the current at a number of selected points in the loop.

At the point P, see figure 1, $x=0$,

I_P $$\therefore\ I_P = I_0 \operatorname{cosech} \tfrac{1}{2}Pl \cosh \tfrac{1}{2}Pl = I_0 \coth \tfrac{1}{2}Pl \qquad \text{.....(3).}$$

At the point P', $x=\frac{1}{2}l$,

$I_{P'}$ $$\therefore\ I_{P'} = I_0 \operatorname{cosech} \tfrac{1}{2}Pl \qquad \text{.....(4).}$$

Equations* (3) and (4) give respectively the variation in the amplitude of the current at the points P and P' as the wave-length is changed. The experimental verification of these expressions is difficult because if the loop be used as a receiver the radiation field must be kept constant as the wave-length changes, and this is sometimes impossible except over a very limited range of wave-lengths. For this reason it is desirable to calculate a theoretical expression for the current ratio $I_P/I_{P'}$, and then the experimental value of this ratio will be independent of the absolute values of the currents, and therefore of the field which produces them. Consequently the experimental value of this ratio may be compared with the theoretical value even though the field-strength varies slightly with change of wave-length.

From equations (3) and (4)

$$\begin{aligned} I_P/I_{P'} &= \cosh \tfrac{1}{2}Pl \\ &= \cosh \tfrac{1}{2}(\alpha + j\beta)\, l \\ &= \cosh \tfrac{1}{2}\alpha l \cos \tfrac{1}{2}\beta l + j \sinh \tfrac{1}{2}\alpha l \sin \tfrac{1}{2}\beta l \end{aligned} \qquad \text{.....(5).}$$

The graph of this equation can be plotted by considering each expression separately, and then adding the two expressions together vectorially. This has been done and is shown by the full-line graph in figure 3. If damping be neglected, i.e. if $\alpha=0$, the equation becomes

$$I_P/I_{P'} = \cosh \tfrac{1}{2}j\beta l = \cos \tfrac{1}{2}\beta l \qquad \text{.....(6)*.}$$

The graph of equation (6) is given in figure 3 by the dotted curve, and it is apparent that the effect of damping is to raise the value of the current ratio $I_P/I_{P'}$ by $\cosh \frac{1}{2}\alpha l$

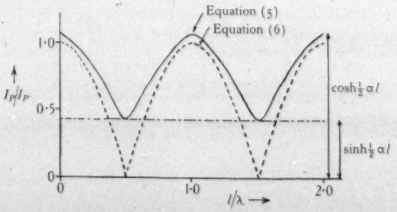

Figure 3. The variation of $I_P/I_{P'}$ with wave-length.

when $l/\lambda = 0$, 1·0, 2·0, etc., and by $\sinh \frac{1}{2}\alpha l$ when $l/\lambda = 0{\cdot}5$, 1·5, 2·5, etc., although the general shape of the graph is similar to that obtained if damping is neglected.

* If damping be neglected these expressions become $I_P = I_0 \cot \frac{1}{2}Pl$ and $I_{P'} = I_0 \operatorname{cosec} \frac{1}{2}Pl$, which follow directly from equation (5) of the previous paper[2].

The experiments which were carried out to test the above theory will now be considered.

§ 4. EXPERIMENTAL WORK

Experiments were carried out with a circular loop aerial of perimeter 11·3 m. The aerial wire was carried on suitable insulators attached to the supporting framework, and the framework itself was fixed on rollers so arranged that the aerial could be rotated about a fixed central axis. The current was measured by means of a

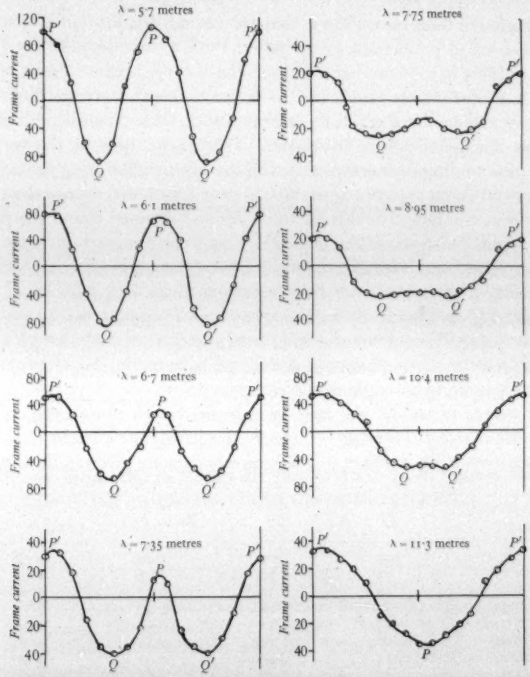

Figure 4. The current-distribution in a circular loop aerial of perimeter 11·3 m., with various wave-lengths.

vacuum thermojunction and a microammeter. Where the thermojunction was inserted in the loop, the aerial wire was shunted by a condenser of capacity 0·0005 μF. which tuned that portion of the loop to the wave-length in use. The current in the shunted portion of the aerial wire varied in the same way as that in adjacent parts of the loop but was of greater magnitude, and was consequently easier to measure. The thermojunction was connected by a short length of flex to a microammeter which rested on a small platform attached to the frame.

The transmitter consisted of an ordinary series-fed Hartley circuit. To this was coupled a Hertzian dipole aerial of adjustable length. In the actual experiments the transmitter was arranged several wave-lengths away from the receiving loop, the current in which was measured at various points along the perimeter. Figure 4 shows a series of results obtained in this way, with wave-lengths varying from 5·7 to 11·3 m.

§ 5. DISCUSSION OF RESULTS

Examination of these curves shows that the current-distribution is in accordance with the theoretical predictions given in § 2. With a wave-length of 5·7 m., four peaks occur. This is to be anticipated from the theory, because under these conditions l/λ is approximately equal to 2. As the wave-length increases the magnitude of the current at the point P gradually decreases until, with a wave-length of 7·35 m., the peak at this point almost disappears. Further increase of the wave-length causes the peak to disappear completely, and the two neighbouring peaks Q and Q' move closer and closer together until, with a wave-length of 11·3 m., the two peaks merge into one, and only two current antinodes are obtained round the perimeter, one at the point P and one at the point P'. This transition with increase of wave-length is in accordance with the theory. The current antinodes at Q and Q' are always $\frac{1}{2}\lambda$ from P' measured round the perimeter of the loop, and hence the antinodes at Q and Q' will gradually move further from P' until, when $l/\lambda = 1$, only the antinodes at P and P' are obtained. Still further increase of wave-length causes the current antinode at P to disappear again, and eventually the current becomes approximately uniform throughout the entire loop.

These current-variations will now be compared with those predicted by the theory developed in § 3. This may be done by calculating the current ratio $I_P/I_{P'}$ for each of the curves given in figure 4. The requisite data are given in the table below.

Wave-length λ (metres)	I_P	$I_{P'}$	Ratio $I_P/I_{P'}$	l/λ
5·7	106	100	1·06	1·98
6·1	72	76	0·95	1·91
6·7	56	32	0·57	1·68
7·35	34	16	0·47	1·54
7·75	23	12	0·52	1·46
8·95	23	19	0·82	1·26
10·4	52	48	0·92	1·09
11·3	37	36	1·03	1·00

In figure 5 the experimental values of $I_P/I_{P'}$ are plotted against l/λ, and on the same graph the theoretical curve given by equation (5) has been plotted with an attenuation constant equal to 0·073 per metre.

§ 6. CONCLUSIONS

The results of the above experiments seem to constitute further evidence in support of the theory outlined in this paper and in the previous communication,

both with regard to the positions round a loop aerial at which current antinodes occur, and also with regard to the magnitude of the amplitude-variations which occur with changes of wave-length. Furthermore it has been shown that with these

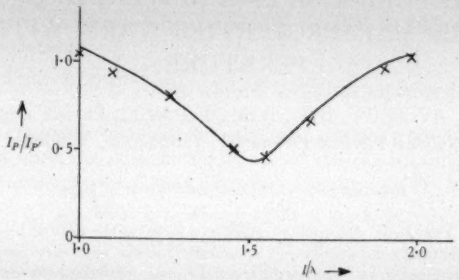

Figure 5. Experimental values (crosses) of the ratio $I_P/I_{P'}$ compared with the theoretical values from equation (5) (smooth curve).

short waves it is necessary to take damping into consideration if the theoretical calculations are to be comparable with the experimental measurements.

Hence it is concluded that equation (2) gives the positions as well as the magnitudes of the current antinodes round a short-wave loop aerial actuated by an e.m.f. located at one point, and this equation may be used for calculating the current-distribution in a loop aerial when the wave-length and position of the applied e.m.f. are known.

§ 7. ACKNOWLEDGMENT

Finally my most sincere thanks are due to Prof. L. S. Palmer for continual interest and invaluable suggestions during the course of the work.

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536.21

TEMPERATURE-RISE IN A MATERIAL OF WHICH THE THERMAL PROPERTIES VARY WITH TEMPERATURE

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ABSTRACT. The partial differential equations governing the flow of heat in a medium for which the thermal conductivity and volumetric specific heat vary parabolically with temperature is reduced to an ordinary differential equation for the case when the medium is semi-infinite in extent. The equation is solved exactly for the case where the two properties vary proportionally to each other, and approximately, in powers of $x/\sqrt{(2t)}$, where x is the distance from the hot face and t the time, for the general case.

§ 1. INTRODUCTORY

The fundamental equation for the temperature-distribution in a material of which the thermal conductivity and specific heat vary with temperature is found, by the usual process of equating the net heat-inflow over the boundaries of an element of volume to the product of the temperature-rise and heat-capacity, to be

$$c\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial x}\left(K\frac{\partial\theta}{\partial x}\right)+\frac{\partial}{\partial y}\left(K\frac{\partial\theta}{\partial y}\right)+\frac{\partial}{\partial z}\left(K\frac{\partial\theta}{\partial z}\right) \qquad \text{.....(1),}$$

θ, t, K, c where θ is the temperature at time t and at the point (x, y, z), K is the thermal conductivity and c the specific heat per unit volume.

This equation is non-linear, and hence it is impossible to obtain a general solution by the addition of particular solutions. Thus the solution adapted to any but the very simplest boundary conditions would be overwhelmingly difficult to obtain. Nevertheless, it appears of interest to consider in detail some specific case in order to ascertain the relative importance of the various factors involved. From such an analysis, it should be possible to assess, in other more complicated cases, what deviation from the simple solution pertaining to unvarying properties is to be expected.

§ 2. REDUCTION TO AN ORDINARY DIFFERENTIAL EQUATION

The simplest case which suggests itself is that of the one-dimensional flow of heat in a large mass of material initially at the uniform temperature θ_0, the plane face of which is raised when the time $t=0$ to a temperature θ_1 and maintained at

this temperature thereafter. We take this plane to be the plane $x=0$, and the equation reduces to x

$$c\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial x}\left(K\frac{\partial\theta}{\partial x}\right) \qquad \text{.....(2).}$$

It is known that, if K and c are independent of θ, the solution of this equation under the conditions stated is

$$\theta=\theta_1+\frac{2(\theta_0-\theta_1)}{\sqrt{\pi}}\int_0^{x/2h\sqrt{t}}e^{-\beta^2}d\beta, \text{ where } h^2 \text{ is the thermal diffusivity } K/c. \quad h$$

Adopting the suggestion contained in this solution, we take a new variable y equal to $x/(2t)^{\frac{1}{2}}$ and transform equation (2) by its aid into an ordinary, instead of a partial, differential equation, θ becoming a function of y only. We have y

$$\frac{\partial\theta}{\partial t}=-\frac{x}{(2t)^{\frac{3}{2}}}\frac{\partial\theta}{\partial y} \quad \text{and} \quad \frac{\partial\theta}{\partial x}=\frac{1}{(2t)^{\frac{1}{2}}}\frac{\partial\theta}{\partial y},$$

so that equation (2) becomes

$$-\frac{xc(\theta)}{(2t)^{\frac{3}{2}}}\frac{d\theta}{dy}=\frac{1}{(2t)^{\frac{1}{2}}}\frac{d}{dy}\left[K(\theta)(2t)^{-\frac{1}{2}}\frac{d\theta}{dy}\right],$$

i.e. $$-\frac{xc(\theta)}{(2t)^{\frac{1}{2}}}\frac{d\theta}{dy}=K(\theta)\frac{d^2\theta}{dy^2}+\frac{dK}{d\theta}\left(\frac{d\theta}{dy}\right)^2 \quad \text{since} \quad \frac{dK(\theta)}{dy}=\frac{dK(\theta)}{d\theta}\frac{d\theta}{dy}.$$

The equation for θ as a function of y is thus

$$yc\,d\theta/dy+K\,d^2\theta/dy^2+(dK/d\theta)(d\theta/dy)^2=0 \qquad \text{.....(3),}$$

where c, K and $dK/d\theta$ are functions of θ.

§ 3. FURTHER REDUCTION TO A PARTICULAR CASE

It does not seem possible to solve this equation in general, and empirical expressions for K and c as functions of θ must therefore be introduced. It is probably sufficiently general if we write

$$c=c_0(1+\alpha\theta+\beta\theta^2) \quad \text{and} \quad K=K_0(1+\gamma\theta+\delta\theta^2). \qquad c_0, K_0, \alpha, \gamma$$

Equation (3) then takes the form

$$yc_0(1+\alpha\theta+\beta\theta^2)\,d\theta/dy+K_0(1+\gamma\theta+\delta\theta^2)\,d^2\theta/dy^2+K_0(\gamma+2\delta\theta)(d\theta/dy)^2=0.$$

From the point of view of dimensional homogeneity it is preferable to make a further substitution and put y equal to h_0z, where $h_0^2=K_0/c_0$, since the new variable z is dimensionless. The equation then becomes h_0, z

$$z(1+\alpha\theta+\beta\theta^2)\theta'+(1+\gamma\theta+\delta\theta^2)\theta''+(\gamma+2\delta\theta)\theta'^2=0 \qquad \text{.....(4).} \quad \theta'$$

where primes denote differentiations with respect to z.

§ 4. EXACT SOLUTION IN A PARTICULAR CASE

This equation is still intractable, and apparently can only be solved by approximate methods. Before carrying out this process, however, it is interesting to notice that it can be solved exactly in one case, namely if the conductivity and specific

heat both vary linearly at the same rate, so that the diffusivity remains constant. In these circumstances $\beta=\delta=0$, whilst $\alpha=\gamma$. Thus equation (4) reduces to

$$(z\theta'+\theta'')\,(1+\alpha\theta)+\alpha\theta'^2=0.$$

The quantity $e^{z^2/2}$ is an integrating factor for this equation. On multiplying the latter by its integrating factor, we can write it

$$\frac{d}{dz}\left[e^{z^2/2}\,(1+\alpha\theta)\,\theta'\right]=0,$$

i.e.

$$(1+\alpha\theta)\,d\theta=Ae^{-z^2/2}\,dz,$$

A, B whence

$$(1+\alpha\theta)^2/2\alpha=B+A\int_0^z e^{-z^2/2}\,dz \qquad \text{.....(5),}$$

which gives an explicit expression for θ as a function of z, where $z=x/h_0\,(2t)^{\frac{1}{2}}$.

It is of distinct interest to notice that although the diffusivity is constant, the temperature-distribution differs from that which is obtained when the conductivity and specific heat separately are constants.

§ 5. SOLUTION IN THE GENERAL CASE

In the general case, equation (4) must be solved by approximate methods. Since it is of the second order there are two arbitrary constants in the solution. *λ* These we fix by writing $\theta=0$ when $z=0$ and $d\theta/dz=\lambda$ when $z=0$.

Successive differentiations of equation (4) with respect to z give a series of equations of which the fourth is

$$\begin{aligned}16\,(\alpha+2\beta\theta)\,\theta'\theta'''+4\,(1+\alpha\theta+\beta\theta^2)\,\theta^{\mathrm{iv}}+48\beta\theta'^2\theta''+30\beta z\theta'\theta''^2\\+20\beta z\theta'^2\theta'''+12\,(\alpha+2\beta\theta)\,\theta''^2+10z\,(\alpha+2\beta\theta)\,\theta''\theta'''+5z\,(\alpha+2\beta\theta)\,\theta'\theta^{\mathrm{iv}}\\+z\,(1+\alpha\theta+\beta\theta^2)\,\theta^{\mathrm{v}}+30\delta\theta''^3+120\delta\theta'\theta''\theta'''+30\delta\theta'^2\theta^{\mathrm{iv}}+10\,(\gamma+2\delta\theta)\,\theta'''^2\\+15\,(\gamma+2\delta\theta)\,\theta''\theta^{\mathrm{iv}}+6\,(\gamma+2\delta\theta)\,\theta'\theta^{\mathrm{v}}+(1+\gamma\theta+\delta\theta^2)\,\theta^{\mathrm{vi}}=0.\end{aligned}$$

Inserting the boundary conditions into these equations in turn, and using the subscript zero for values at $z=0$, we find that

$$\theta_0=0,\qquad \theta_0'=\lambda,\qquad \theta_0''+\gamma\lambda^2=0,$$

$$\lambda+3\gamma\lambda\theta_0''+\theta_0'''+2\delta\lambda^3=0,$$

$$2\alpha^2+2\theta_0''+12\delta\lambda^2\theta_0''+3\gamma\theta_0''^2+4\gamma\lambda\theta_0'''+\theta_0^{\mathrm{iv}}=0,$$

$$3\theta_0'''+6\beta\lambda^3+9\alpha\lambda\theta_0''+30\delta\lambda\theta_0''^2+20\delta\lambda^2\theta_0'''+10\gamma\theta_0''\theta_0'''+5\gamma\lambda\theta_0^{\mathrm{iv}}+\theta_0^{\mathrm{v}}=0,$$

$$\begin{aligned}16\alpha\lambda\theta_0'''+4\theta_0^{\mathrm{iv}}+48\beta\lambda^2\theta_0''+12\alpha\theta_0''^2+30\delta\theta_0''^3+120\delta\lambda\theta_0''\theta_0'''\\+30\delta\lambda^2\theta_0^{\mathrm{iv}}+10\gamma\theta_0'''^2+15\gamma\theta_0''\theta_0^{\mathrm{iv}}+6\gamma\lambda\theta_0^{\mathrm{v}}+\theta_0^{\mathrm{vi}}=0.\end{aligned}$$

These equations can now be solved for the successive derivatives of θ, giving

$$\theta_0=0,\quad \theta_0'=\lambda,\quad \theta_0''=-\gamma\lambda^2,\quad \theta_0'''=-\lambda+(3\gamma^2-2\delta)\,\lambda^3,$$

$$\theta_0^{\mathrm{iv}}=(6\gamma-2\alpha)\,\lambda^2+(20\gamma\delta-15\gamma^3)\,\lambda^4,$$

$$\theta_0^{\mathrm{v}}=3\lambda+(26\delta-49\gamma^2-6\beta+19\alpha\gamma)\,\lambda^3+(40\delta^2-210\gamma^2\delta+105\gamma^4)\,\lambda^5,$$

$$\begin{aligned}\theta_0^{\mathrm{vi}}=(24\alpha-52\gamma)\,\lambda^2+(92\alpha\delta+84\beta\gamma-576\gamma\delta+504\gamma^3-204\alpha\gamma^2)\,\lambda^4\\+(2520\gamma^3\delta-945\gamma^5-1120\gamma\delta^2)\,\lambda^6.\end{aligned}$$

The final solution valid for sufficiently small values of z is then obtained from Maclaurin's theorem by substituting the above values of $\theta_0^{(r)}$ in the expression

$$\theta=\theta_0+z\theta_0'+\frac{z^2}{2!}\theta_0''+\frac{z^3}{3!}\theta_0'''+\frac{z^4}{4!}\theta_0^{\mathrm{iv}}+\frac{z^5}{5!}\theta_0^{\mathrm{v}}+\frac{z^6}{6!}\theta_0^{\mathrm{vi}}+\ldots.$$

If the terms are rearranged in powers of λ, this expression becomes

$$\theta=\lambda\left[z-\frac{z^3}{6}+\frac{z^5}{40}+\ldots\right]+\text{terms in } \lambda^2, \lambda^3, \ldots.$$

The expression in the bracket represents the expansion of $\lambda\int_0^z e^{-z^2/2}dz$, i.e. the temperature which would be reached in the case where the thermal constants are independent of temperature.

Thus the result reached might be written in the form

$$\theta=\lambda\int_0^z e^{-z^2/2}dz+\text{terms in } \lambda^2, \lambda^3, \ldots,$$

the terms after the first representing the disturbance in θ due to the variation of the thermal conductivity and specific heat with temperature. It is worthy of note that the variation of the conductivity has a much greater effect than that of the specific heat; this is evidenced by the fact that α and β are absent from the terms in λ^2z^2 and in λ^3z^3, the former first making its appearance in the term in λ^2z^4 and the latter in λ^3z^5.

§ 6. NUMERICAL ILLUSTRATION

As an illustration we take the case of a brick for which $h_0^2=0{\cdot}0020$ and both specific heat and thermal conductivity increase by 1 per cent per 1° C. The final temperature, reached when $z=0$, is taken as the zero of temperature, and the rise at the hot face is determined by $\lambda=200/\sqrt{(2\pi)}$, which makes the dominating term reduce to the value 100 when $z=\infty$. Thus the initial temperature would be 100° C. if there were no variation of the thermal constants with temperature. The whole expression in this case reduces to

$$\theta=\frac{200}{\sqrt{(2\pi)}}\int_0^z e^{-z^2/2}dz-\frac{100}{\pi}z^2+\frac{79{\cdot}95z^3}{\pi}+\frac{33{\cdot}33z^4}{\pi}-\frac{250z^4}{\pi^2}-\frac{39{\cdot}9z^5}{\pi}$$
$$+\frac{279{\cdot}4z^5}{\pi^2}-\frac{7{\cdot}778z^6}{\pi}+\frac{166{\cdot}67z^6}{\pi^2}-\frac{1050z^6}{\pi^3}+\ldots$$
$$=\frac{200}{\sqrt{\pi}}\int_0^{z/\sqrt{2}}e^{-x^2}dx-31{\cdot}831z^2+25{\cdot}43z^3-14{\cdot}74z^4+15{\cdot}63z^5-19{\cdot}45z^6+\ldots.$$

The numerical values calculated from this formula are given in table 1 for a selection of values of z. The expansion is only convergent for $z<1$ and appears to be of adequate accuracy up to about $z=0{\cdot}6$; beyond this point it would be necessary to carry it to higher powers of z.

Table 1

z	$\frac{200}{\sqrt{\pi}}\int_0^{z/\sqrt{2}} e^{-x^2}dx$	Sum of remaining terms
0·005	0·40	−0·00079
0·01	0·80	−0·00316
0·02	1·60	−0·0125
0·05	3·99	−0·0765
0·10	7·97	−0·2943
0·20	15·85	−1·090
0·40	31·08	−3·76
0·60	45·14	−7·5$_6$

It will be seen that the deviation in the temperature-distribution does not become 1 per cent of the whole temperature-rise until $z=0{\cdot}02$.

With a value 0·0020 of $h_0{}^2$, a typical value for a refractory material, this occurs when $x/\sqrt{t}=0{\cdot}06$. Thus at a depth of 5 cm. no deviation will exist after about $1\frac{1}{2}$ hours, whilst conversely, after say 4 hours, the deviation is only to be found at distances from the hot face greater than 7 cm.

It is also worthy of remark that the values of the temperature calculated by means of the series expansion are hard to compare directly with those obtained from the exact formula (5) which applies to this case.* This arises from the fact that the series expansion is divergent beyond $z=1$, and consequently the constant λ cannot be adjusted to give a specified range of temperature; only the dominant term can be caused to vary over a selected range, and thus the solution represented by the series in fact covers some slightly different range. In the case of the exact solution the adjustment of the constants A and B causes the actual temperature to vary over the range desired.

Nevertheless it is of interest to compare the exact solution with that tabulated above. In table 2, the constant B of equation (5) has been taken as 50, and three values—100, 106·2 and 114·5—have been assigned to $A\sqrt{(\pi/2)}$.

Table 2. Temperature as function of z, where $z=x/h_0\sqrt{(2t)}$

z	Temperature			
	By series expansion	By formula (2), $A\sqrt{(\pi/2)}$ being taken as		
		106·2	114·5	100
0·005	0·40	0·4	0·4	0·40
0·01	0·80	0·8	0·9	0·80
0·02	1·59	1·7	1·8	1·60
0·05	3·92	4·1	4·5	3·99
0·10	7·70	8·1	8·7	7·67
0·20	14·76	15·6	16·8	14·76
0·40	27·32	28·8	30·8	27·43
0·60	37·58	40·0	42·6	37·92

* See, however, the author's reply to the discussion, page 124.

§ 7. CONCLUSIONS

Although the illustrative example just given is one in which the variation of both properties is relatively rapid, yet the deviations from the case of constant diffusivity are fairly small. This may in part be due to the fact that the specific heat and thermal conductivity in this example are proportional to each other, so that their ratio remains constant.

We therefore take another example less likely to be encountered in practice, in which the specific heat increases by 1 per cent per 1° C., but the conductivity decreases by 1 per cent per 1° C.

In this case, the series formula becomes

$$\theta = \frac{200}{\sqrt{\pi}} \int_0^{z/\sqrt{2}} e^{-x^2} dx - 31{\cdot}831z^2 + 25{\cdot}43z^3 + 4{\cdot}11z^4 - 0{\cdot}47z^5 + 0{\cdot}75z^6 \ldots,$$

and the sum of the last five terms varies with z in the way shown in table 3.

Table 3

z	Sum of terms other than dominating term
0·005	−0·00079
0·01	−0·0032
0·02	−0·0125
0·05	−0·0764
0·10	−0·292
0·20	−1·064
0·40	−3·36
0·60	−5·43

Here also, the deviations from the case of constant diffusivity are fairly small, and it seems therefore reasonable to assume that a similar result would hold in the cases likely to be encountered in practice.

DISCUSSION

Mr C. R. DARLING said that the paper had a bearing on the problem of the time taken by the centre of a block of metal in a furnace to attain a steady temperature. Experimenting with thermocouples on cylindrical blocks of steel he had found that the time varied as the square of the diameter; this appeared to agree with Mr Awbery's conclusions.

Mr E. D. VAN REST. I am sometimes asked to make calculations of the rise of temperature inside a piece of wood when it is subject to given external conditions, for instance in a drying chamber. My early measurements of thermal diffusivity were not entirely in agreement with theory and at one time I thought that the discrepancies might be due to a temperature variation of the diffusivity. This proved not to be the case, for fair agreement with theory was later obtained. This

is in accord with the author's findings that the temperature variation does not cause large differences. I am interested, too, in the conclusion arrived at in § 2 where the author shows that the same proportionate variation in conductivity and specific heat, while not affecting their ratio, the diffusivity, does affect the temperature-distribution. The conclusion is, I suppose, that measurements of the temperature variation of diffusivity cannot be used to calculate how the temperature-distribution differs from that predicted from simple theory, but must give place to separate measurements of conductivity and specific heat. With wood, one of the difficulties in applying theory to practice is the probably large variation of diffusivity with moisture-content combined with the uneven distribution of moisture during drying.

AUTHOR'S reply. In reply to Mr Darling and Mr van Rest, I am interested to learn that their experiments are not in contradiction to the theory. Fortunately, the practical importance of the point raised in § 2 is small, since the numerical calculations show that the deviation of the temperature-distribution from that given by simple theory is never likely to become serious.

I am indebted to Prof. Davidson for pointing out an algebraical error which affects the numerical values in tables 1, 2 and 3 as printed in the advance proofs. The necessary corrections have now been made.

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A NEGATIVE-RESISTANCE OSCILLATOR

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ABSTRACT. It is shown that an amplifier with its input and output terminals connected together can behave as a negative resistance. This principle leads to the design of an oscillator employing two triodes, and having certain advantages over both the ordinary reaction circuit and the screen-grid dynatron. Some special wave-forms which were observed are illustrated. A method of using the instrument to measure the dynamic resistance of an oscillatory circuit is suggested.

§ 1. INTRODUCTION

Methods of generating electrical oscillations by means of thermionic valves may be divided broadly into two classes. In the first class are the reaction methods in which some coupling is provided between the grid and anode circuits. This is often a mutual-inductance coupling or reaction coil, but we may also include in the same class methods in which the coupling is effected by using a tapping on the tuning inductance, or by splitting the tuning condenser into two condensers in series. The second class consists of the negative-resistance methods, in which use is made of the fact that under certain conditions a pair of electrodes can be found for which the curve of current against voltage has a negative slope over part of its range, so that the system is capable of delivering power to an external circuit. The phenomenon of secondary emission causes the plate current of a triode to follow a curve of this sort when the grid is maintained at a large positive potential with respect to the filament. A valve used in this way is usually known as a *dynatron*.

In the case of a reaction circuit the operation of the valve in conjunction with any given coupling can be represented by means of an oscillation characteristic having a negative slope[1]. Analytically therefore the two classes are similar, and there is no fundamental distinction between them. There is however an important difference in practice. In the second class of circuit the valve and its associated apparatus, such as batteries, can be connected to the oscillatory circuit proper by two leads only, without the complications of reaction coils, tapped inductances or split condensers. This is particularly convenient when operation is required over a wide range of frequencies, since the number of connexions to be changed and adjustments to be made is reduced to a minimum.

When a triode is used as a dynatron the large potential which must be applied to the grid produces a very large emission current. This results in a heavy consumption of power, overheating of the grid, and deterioration of the emitting surface; this last effect is particularly serious in the case of the oxide-coated cathodes used in

modern valves. It is therefore usual to employ a screen-grid valve with the outer or screening grid maintained at a high positive potential and the inner or control grid connected to the filament or cathode. This arrangement is deservedly popular, but suffers nevertheless from several disadvantages. Thus (i) the valve usually has to be specially selected; (ii) the working conditions are fairly critical and apt to vary with time; (iii) it is not possible to obtain low values of negative resistance, so that the oscillatory circuits must be of low damping; (iv) two separate high-tension voltages are required; (v) the oscillatory circuit is at a high d.-c. potential with respect to the filament; and (vi) the d.-c. component of the anode current passes through the inductance of the oscillatory circuit, which is objectionable if iron-cored inductances are to be used.

The circuit to be described makes use of two valves, which can be triodes, operating under normal amplifying conditions. It has the advantages of the negative-resistance type of oscillator without the above-mentioned disadvantages of the screen-grid dynatron.

A circuit using two triodes to give a negative resistance effect has been described under the name of *kallirotron* by L. B. Turner[2]. It is unsuitable for general use as an oscillation-generator, since it makes use of five batteries at different oscillatory potentials. Again, a circuit apparently very similar to that described below has been used by C. S. Franklin as the master-oscillator of short-wave transmitters[3]. The present paper shows how the fundamental principle made use of by Turner and by Franklin can be applied to the design of a universal oscillator which can operate at any desired frequency, and in which the magnitude of the negative-resistance effect is completely under control.*

§ 2. THE AMPLIFIER AS A NEGATIVE RESISTANCE

Figure 1 represents an amplifier with input terminals a, b and output terminals c, d. It is assumed that the internal connexions are such that one of the input and

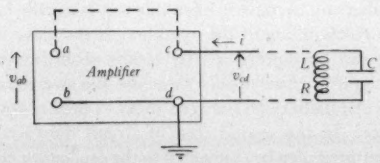

Figure 1. An amplifier used as a negative resistance.

one of the output terminals are held at the same potential, and the points b, d are accordingly shown connected together and to earth. The dotted lines should be ignored for the moment.

* During the preparation of this paper, a paper on "A negative-resistance device and its application to harmonic analysis" was read by Mr C. W. Oatley before the Physical Society, *Proc. phys. Soc.* **47**, 471 (1935). The present author's arrangement can of course be used for the same purpose as Mr Oatley's, and it appears to have some practical advantages over his circuit.

If v_{ab}, v_{cd} are the input and output voltages, and i the current flowing from d to c through an external circuit, we have for an "ideal" amplifier the relation v_{ab}, v_{cd}, i

$$v_{cd} = Mv_{ab} + R_0 i \qquad \text{.....(1)},$$

where M and R_0 are constants characteristic of the amplifier, viz. the voltage amplification factor and the output impedance. In other words, the amplifier is equivalent to a battery or generator of e.m.f. Mv_{ab} and internal resistance R_0, the equivalent circuit being as in figure 2. M, R_0

If there is no voltage applied to the input, so that $v_{ab} = 0$, the amplifier behaves with respect to the external circuit connected to cd as a simple resistance of magnitude R_0. Now let the input and output terminals be connected together, as shown by the dotted line in figure 1, so that $v_{ab} = v_{cd}$. We now have

$$v_{cd}(1 - M) = R_0 i \qquad \text{.....(2)},$$

showing that the amplifier now behaves with respect to the external circuit as a simple resistance of magnitude $R_0/(1 - M)$. If we imagine M increased from zero

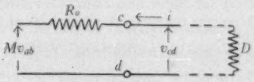

Figure 2. Equivalent circuit of the amplifier.

the value of this resistance will increase from R_0, becoming infinite when $M = 1$; when $M > 1$ it becomes negative in sign, which means that power is supplied to the external circuit instead of being absorbed from it.

Suppose the external circuit is that shown in figure 1, namely an oscillatory circuit consisting of a coil of inductance L in parallel with a condenser of capacity C, the equivalent series resistance of the circuit at any given frequency being R. Then, as the value of M is increased, the damping of the oscillatory circuit will be reduced, and will become zero when

$$\frac{R_0}{1 - M} = -D \qquad \text{.....(3)},$$

where $D = L/CR$ and is the *dynamic resistance* of the circuit at its resonant frequency. This is therefore the condition for the maintenance of oscillations. D

This result can also be reached from a slightly different viewpoint, as follows. Consider once more the amplifier in figure 1 without the connexion between c and a, but with the oscillatory circuit connected across the output terminals cd. Let a voltage v_{ab} varying sinusoidally at a frequency equal to the resonant frequency of the oscillatory circuit be applied to the input terminals ab. Then it is clear from the equivalent circuit of figure 2 that the output voltage v_{cd} will be equal to $M'v_{ab}$, where

$$M' = M\frac{D}{R_0 + D} \qquad \text{.....(4)}. \qquad M'$$

If $M' = 1$ the source of the input voltage can be removed and c can be connected to a without affecting the oscillations, which then become self-maintaining. The con-

dition for maintenance is thus found by putting $M'=1$ in equation (4), which then reduces to equation (3).

In the above we have tacitly assumed that a negligible amount of power is consumed at the terminals *ab*; in other words, the input impedance of the amplifier is very great. Otherwise, the effect of connecting this impedance across *cd* must be allowed for. It can easily be shown that the result of connecting a resistance R_1 in parallel with the output terminals of an amplifier is to reduce the effective values of both R_0 and M by the factor $R_1/(R_0+R_1)$. In the present instance R_1 is the input impedance, and the amended values of R_0 and M should be used in calculating the value of the negative resistance and the condition of maintenance.

R_1

§ 3. EFFECT OF AN AMPLIFIER WHICH IS NOT IDEAL

In practice equation (1) will not hold for all values and all modes of variation of the currents and voltages, owing to the effects of inductance and capacity in the amplifier and of non-linearity of the valve characteristics.

Non-linearity of the valve characteristics. If the device is to be used to reduce the damping of a circuit in which forced oscillations are being induced from an external source, the effects of non-linearity can be made as small as desired. It is only necessary to use valves and potentials which are such that the working point does not pass beyond the limits of that part of the characteristic which can be regarded as a straight line. This condition is, of course, that which leads to the absence of wave-form distortion in an ordinary amplifier.

The case of self-generated oscillations is somewhat different. The assumption of a perfectly linear characteristic in this case would be an over-simplification. It would imply that if the maintenance condition were exactly satisfied an oscillation of any amplitude whatever once set up in the circuit would be maintained at that amplitude; moreover, the slightest departure from this condition, such as might be caused for instance by a small change in battery voltage, would result in the amplitude either decreasing to zero or increasing indefinitely. In practice, however, we find that a given circuit condition corresponds to a definite amplitude of the oscillation, and that a small change in this condition merely causes the amplitude to change to one of a different value. This can only be explained by taking account of the curvature of the valve characteristics, which makes the circuit constants (i.e. M and R_0 in the case with which we are concerned) dependent upon the amplitude. Thus, at infinitesimal amplitudes the effective resistance of the oscillatory circuit will be slightly negative. Any small oscillation will therefore grow until it attains an amplitude at which the effective resistance is reduced to zero; the amplitude will then remain constant at this value.

The very existence of a stable, finite amplitude of oscillation thus depends upon the non-linearity of the characteristic, and consequently implies some departure, however slight, from a purely sinusoidal wave-form. If it is desired to keep the wave-form as pure as possible, an oscillator should be operated at a point only just beyond that at which oscillations commence. To enable this to be done it is essential

to have some means of control which can produce a gradual and continuous variation of the negative-resistance effect. In the circuit described below this takes the form of a potential-divider controlling the value of the amplification M.

Inductance and capacity in the amplifier. In the case of approximately sinusoidal oscillations we can represent the behaviour of the amplifier at a particular frequency by assigning complex values to M and R_0.

As far as R_0 is concerned this effect can usually be represented by a small capacity in parallel with the output terminals; this capacity can be incorporated in the value of C, and need not concern us further.

The effect of a complex value of M, corresponding to a phase-displacement in the amplifier, is to cause a shift of the frequency to a new value at which the oscillatory circuit no longer behaves as a pure resistance. Fortunately, since the phase angle of the impedance of an oscillatory circuit changes very rapidly with frequency near the point of resonance, only a small frequency-shift is required to compensate for quite a large phase-displacement in the amplifier. This can be shown as follows.

If x is the fractional change in frequency from resonance and δ the decrement, the impedance Z of the oscillatory circuit is given by[4] x, δ Z

$$\frac{1}{Z}=\frac{1}{D}\left(1-j\frac{2\pi x}{\delta}\right) \qquad \text{.....(5).}$$

Replacing D by Z in equation (4), putting $M=a\,(1-j\tan\phi)$ and inserting the condition $M'=1$, we find that a, ϕ

$$x=\frac{\delta}{2\pi}\left(\frac{R_0+D}{R_0}\right)\tan\phi \qquad \text{.....(6).}$$

Normally D will be of the same order of magnitude as R_0, and δ will be a small fraction, so that the fractional change of frequency will not be appreciable unless the phase displacement ϕ exceeds (say) 45°. If the phase-change is due to stray capacity in a single stage, this means that the oscillator will work satisfactorily at all frequencies below that at which the reactance of this stray capacity becomes equal to the resistance with which it is in parallel.

If the amplifier is to act as nearly as possible as a pure negative resistance over a wide frequency-range, inductive couplings are excluded. In a resistance-coupled amplifier however there is a change in phase of 180° in each stage. The amplification M is therefore negative with an odd number of stages and positive with an even number. As far as the magnitude of M is concerned, one stage would be sufficient for all ordinary purposes; but in order to obtain a negative value for the resistance, M must be positive in sign, which makes it necessary to use two stages.

If, however, we were to permit the use of an inductive coupling, this could be made positive or negative as required, and it would become possible to use a single valve. The circuit would then in effect be the ordinary reaction circuit. This illustrates the fact that the distinction between the two classes of circuit is not fundamental.

§ 4. THE DESIGN OF THE OSCILLATOR

In figure 3 is shown a practical circuit for an oscillator based on the principle described above, and intended for use at audio and low radio frequencies. It is derived from a two-valve resistance-capacity-coupled amplifier, the only alterations being the connexion between output and input and the variable potential-divider in the anode circuit of the valve V_1. This potential-divider enables the amplification, and consequently the value of the negative resistance, to be varied as desired; it is thus in effect the reaction coupling of the oscillator. By placing this control in the anode circuit instead of in one of the grid circuits, the effect of stray capacities at high frequencies is minimized.

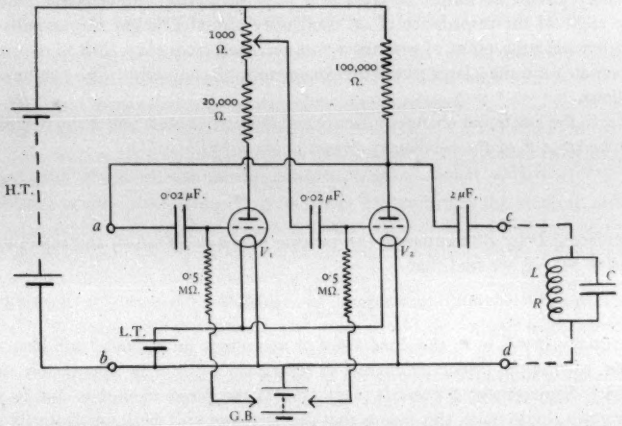

Figure 3. A practical circuit.

As the magnification required is normally much less than the maximum of which a two-stage amplifier is capable, the potential-divider is split into two parts, the variable part having a much lower resistance than the other. The total resistance in the anode circuit is kept high so as to maintain the linearity of the working characteristic of V_1.

It should be observed that with normal settings of the potential-divider the oscillatory potential on the grid of V_2 will be much less than that on the grid of V_1. If the valves are at all similar, therefore, the working portion of the characteristic of V_1 may become considerably curved before that of V_2 departs appreciably from a straight line. Thus it is the characteristic of V_1 which determines the amplitude and wave-form of the oscillations; V_2 may be regarded as a linear coupling device, the main function of which is to produce a change in phase of 180°. It follows that the output, for a given harmonic content, will be of the same order as that which would

be obtained from the valve V_1 if it were used with the same mean operating potentials in a single-valve oscillator of the ordinary kind. It is of course convenient, though not necessary, to use two valves of the same type. The values of the coupling condensers and grid leaks should be such that their time constants are larger than the period of the slowest oscillations with which it is desired to work.

To ensure satisfactory operation at the higher frequencies the resistances used should have the least possible inductance and capacity. Resistances of metallized or composition type used in wireless receivers are suitable. The usual precautions should be taken to avoid stray capacity effects, especially between the grid and anode circuits of the same valve. It is also advantageous to use valves of low impedance.

If the circuit values given in figure 3 are used, the range over which satisfactory operation is obtained should be from less than 100 c./sec. to something like 10^5 c./sec. The range can easily be extended to lower frequencies, if desired, by increasing the values of the coupling condensers or grid leaks, or both. The cost of mica condensers becomes high when capacities greater than $0{\cdot}02\mu$F. are required, but if paper condensers are used care must be taken to see that the insulation resistance is maintained.

If the apparatus is required to operate at radio frequencies it is suggested that valves of the h.-f. pentode type should be used, and a screen interposed between the two sets of components associated with the two valves. The 20,000-ohm resistance in the anode circuit of V_1 should be omitted. Such a design should work well at frequencies up to several million cycles per second, and should be nearly if not quite as effective at low frequencies. On the other hand, the valves are more expensive than triodes, and provision would have to be made for applying a suitable voltage to the screening-grids.

The potentials to be applied are those which would be required by the valves if these were used in a normal amplifier. In fact the design requirements can be conveniently summarized by saying that the apparatus will work well as an oscillator or negative-resistance device over the whole range of frequencies and amplitudes for which it would be satisfactory as an amplifier. For most purposes, therefore, the values of the components are not at all critical.

§ 5. EXPERIMENTAL TEST

In order to test the principle experimentally the necessary modifications were made in an existing three-valve resistance-capacity-coupled amplifier, one of the valves being removed. The circuit used was similar to that shown in figure 3, in which the values of the components are given. The main difference was the presence of a decoupling circuit comprising 20,000 ohms and 2μF. in the anode circuit of V_2. Battery valves were used with a l.-t. supply of 2 V. and h.-t. of 200 V. from accumulators. The wave-form of the potential-difference across the terminals *cd* was observed by means of a cathode-ray oscillograph.

The operation of the device was extremely simple. The biasing potentials were given values which would have been suitable for low-frequency amplification with

the valves in use, and the potential-divider was set for zero amplification. An oscillatory circuit was then connected across *cd* and the amplification was increased until oscillations just commenced.

Oscillatory circuits of widely different natural frequencies were made up from a miscellaneous collection of inductance coils and condensers. Although some of the coils must have had a high resistance, oscillations were produced in every case without difficulty. By the use of iron-cored coils oscillations were obtained at a frequency judged to be as low as 20 c./sec. The wave-form in this case was bad, but the coupling components were not suitable for so low a frequency (see § 4).

In spite of the fact that the apparatus had been designed as a low-frequency amplifier with wire-wound resistances, no difficulty was found in producing oscillations in a circuit resonating at about 6×10^5 c./sec. corresponding to a wave-length of 500 metres.

Various types of valve were tried, such as the Mullard PM2DX, the Osram HL2, and the Mazda P220. All worked satisfactorily, although their characteristics were very different. It was noticed that V_1 had more effect on the behaviour of the oscillator than V_2, in agreement with the considerations put forward in the preceding section.

When the amplification was made only just great enough to produce steady oscillation, the wave-form was not distinguishable by eye from a pure sine wave. Any great increase of the amplification beyond this point caused an appreciable increase in amplitude accompanied by a slight change in frequency and by severe distortion of the wave-form, which assumed a shape reminiscent of a typical relaxation oscillation, somewhat similar to that of figure 4 (*b*). This wave-form distortion was particularly marked, even at low amplitudes, when the ratio of capacity to inductance in the oscillatory circuit was small. It must be pointed out that this kind of behaviour is common to all oscillators, and that the circuit described here is superior to most in this respect owing to the range and smoothness of the control.

Production of special wave-forms. As it often happens that a wave-form is required which has a special shape other than that of a sine wave, it may be of interest to record some observations of particular wave-forms and the conditions under which they were obtained. Those chosen for illustration are shown in figures 4, 5, and 6, which are freehand drawings, not to scale, of the oscillograph images. The direction of the time scale is from left to right in each case, and the alphabetical designations are in order of increasing amplification.

Figure 4 refers to the case in which no external circuit is connected across the terminals *cd*. The circuit becomes unstable when $M > 1$ and generates relaxation oscillations, i.e. oscillations whose period is determined by the times of charging and discharging of the coupling condensers. Figure 4 (*a*) was obtained when the amplification was only just sufficient to cause instability. When the amplification is very great, as in figure 4 (*c*), the circuit is almost identical with that of the multivibrator of Abraham and Bloch, which is used to generate harmonics of high orders for frequency standardization.

Figure 5 illustrates the case when the terminals *cd* are bridged by a condenser

only. This case is particularly interesting, for when the amplification was only just sufficient to produce oscillations these appeared to be of a purely sinusoidal wave-form, although no oscillatory circuit was present. An increase of amplification resulted in a transition to the perfectly triangular form of figure 5 (*a*), and finally to that of figure 5 (*b*).

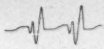

Figure 4.

Figure 5.

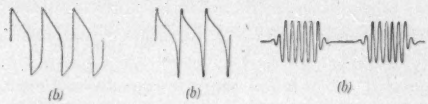

Figure 6.

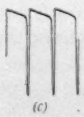

Figure 4. Wave-forms obtained in the absence of an oscillatory circuit.

Figure 5. Wave-forms obtained with a condenser only.

Figure 6. Wave-forms obtained with an inductance only.

Figure 6 shows wave-forms obtained when a large inductance was connected across *cd*. When the amplification was great the oscillations took the form of groups of five or six approximately sinusoidal oscillations of equal amplitude, the groups being separated by intervals of quiescence, as shown in figure 6 (*b*). It is surmised that the period of the individual oscillations corresponded to that of the inductance of the coil in conjunction with its own self-capacity and the stray capacities of the circuit, whereas the period of the groups depended upon the time of charge and discharge of one of the coupling condensers.

§ 6. APPLICATION OF THE INSTRUMENT TO THE MEASUREMENT OF DYNAMIC RESISTANCE

It is suggested that if the potential-divider controlling the amplification were calibrated, the device could be used to find the dynamic resistance of an oscillatory circuit. The method is as follows. The circuit in question is connected between *c* and *d*, and the slider of the potential divider is moved until it reaches the point at which oscillations just commence. Let s be the setting of the slider in this case, i.e. a number proportional to the resistance between the slider and the upper end of the potential-divider. Let s_0 be the value of s which makes M equal to 1; then in general $M=s/s_0$. Therefore from equation (3)

$$D=R_0\frac{s_0}{s-s_0} \qquad \text{.....(7).}$$

R' To find the value of R_0, the process is repeated with a known resistance R' connected in parallel with the oscillatory circuit. Let s' be the setting in this case. Then we have

s'

$$\frac{R_0}{D}=\frac{s}{s_0}-1$$

and

$$R_0\left(\frac{1}{D}+\frac{1}{R'}\right)=\frac{s'}{s_0}-1,$$

whence

$$\frac{R_0}{R'}=\frac{s'-s}{s_0} \qquad \text{.....(8).}$$

To determine s_0, that setting is found which just makes the amplifier unstable with no external circuit connected to c and d. Alternatively the values of s' corresponding to two different values of R' can be found, giving two equations of the form of (8) which can be solved for R_0 and s_0.

This method should be very useful when a number of values of dynamic resistance have to be determined, as for instance in measuring the variation of the dynamic resistance of a circuit with frequency. In such a case R_0 and s_0 can be found once for all, provided the constancy of the batteries and valves can be relied upon.

An endeavour might be made to obtain experimental figures to test the theory given in this section. As the author is not at present in a position to make such an attempt, he publishes the suggestion in the hope that someone with the necessary facilities will find it interesting enough to be worth a trial.

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THE MEASUREMENT OF VERY LOW RELATIVE HUMIDITIES

By A. SIMONS, B.Sc.

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ABSTRACT. Methods available for the measurement of relative humidities lying between 0·5 and 10 per cent are discussed. A dew-point apparatus for measuring dew points down to −40° C. is described, also a hygrometer using wet and dry thermocouples. Calibration curves are given showing the relation between the depression of the wet-junction temperature and the relative humidity over the above range for air-temperatures between 10° C. and 90° C.

§ 1. INTRODUCTION

In the course of certain work it became necessary to measure the moisture-content of air which had been dried by means of the usual drying-agents, such as silica gel, calcium chloride or phosphorus pentoxide. The relative humidity of air which has passed slowly over such a drying-agent is very low indeed, ranging from 0 to about 10 per cent, and its measurement presents rather a different problem from those usually encountered in dealing with humidity-measurements.

Many methods are available for the measurement of humidity, but those which seemed most likely to be of practical use in the region in which it was necessary to work were (*a*) chemical methods, (*b*) the dew-point method, and (*c*) the wet-and-dry-thermocouple method. Chemical methods were tried, but the amount of moisture present was so small that accurate determinations by weighing were difficult to carry out. The time taken to make one measurement was such that a continuous record of the dryness of the air could not be obtained. A volumetric form of chemical hygrometer similar to that described by Griffiths[1] has been used successfully for work at low pressures, but is not suitable for use at atmospheric pressure. The dew-point method was tried and a special apparatus was developed by means of which dew points could be measured down to −40° C. Accurate determinations could be carried out with this apparatus, but in making the observations some skill was necessary to detect the first traces of moisture deposited. It was desired, if possible, to develop an instrument which could be made to record continuously with the minimum amount of skilled care and attention. The method which seemed most likely to be of use from this point of view was that using wet and dry thermocouples.

The theory underlying the use of wet and dry thermocouples for the measurement of humidity is well known and need not be gone into here. The problems which arose in using the method in this particular work were due to the fact that the humidity to be measured was so very much lower than any usually encountered. In consequence, the tables which have been drawn up by various investigators

giving the relationship between the depression of the wet-junction temperature and the humidity of the space at any given temperature did not cover the necessary range, which was from about 10 per cent relative humidity down to 0·5 at atmospheric temperatures.

Accordingly a calibration had to be carried out over the required humidity-range for all the temperatures likely to be encountered in practice. This involved the use of some absolute method of measuring the humidity of the space. The only really absolute methods are chemical methods and the dew-point method. The dew-point method was chosen as being simpler and more accurate, but check determinations by means of weighing were carried out from time to time.

§ 2. APPARATUS USED IN CALIBRATION, AND EXPERIMENTAL PROCEDURE

For the purpose of the calibration the apparatus was enclosed in a chamber with a closely fitting glass front so that it could be maintained at any constant humidity. The seal between the chamber and the glass front was made by means of an inflated rubber tube. Heaters, a cooling-coil and a sensitive thermostat were provided so

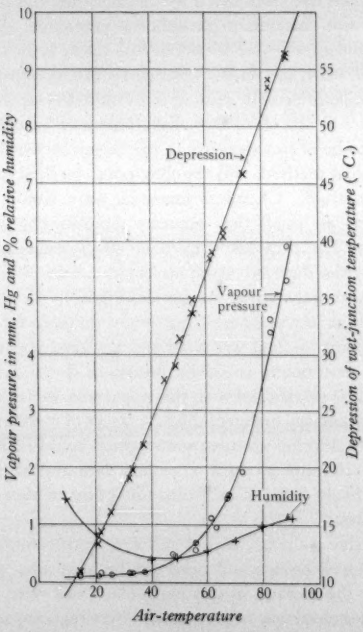

Figure 1. Variation of vapour pressure, relative humidity and depression with temperature.

that readings could be taken at any temperature from about 10° C. to 100° C. A funnel was fixed to one end of the wet-and-dry-thermocouple apparatus so that a current of air could be drawn through it by means of a fan. The relative humidity was measured by the dew-point method, a mirror being inserted through the top of the chamber. A sampling-tube was provided so that samples of air could be drawn off in order to check the dew-point determinations by actual weighing of the moisture-content of the air. The humidity was controlled by solutions of sulphuric acid in porcelain trays at the bottom of the chamber.

The procedure during calibration was to introduce the sulphuric acid, to close the chamber and then to measure the vapour pressure by means of the dew point and the depression of the wet couple, after the fan had been left running for some time to enable stable conditions to be reached. The heaters were then switched on, the thermostat was adjusted to a different temperature and the readings were repeated when the temperature and vapour pressure had again reached equilibrium. This procedure was repeated over the whole range of temperature required. The whole series was then repeated with sulphuric acid solution of a slightly different density. The density of the acid used was varied between 1·40 and 1·84 g./cm.^{3}, seven different concentrations being used.

The curves of vapour pressure and depression against temperature were plotted from the experimental readings, figure 1. The values of the vapour pressure at each 10° C. were read from the curve, and the relative humidity calculated. These values are also shown in figure 1. The corresponding values of relative humidity and depression of wet-couple temperature were thus obtained at each 10° interval over the whole range. From these results curves were plotted showing the relation between the relative humidity and the depression of the wet-junction temperature at a fixed air-temperature. The final smoothed curves are given in figure 6.

§ 3. DEW-POINT APPARATUS USED FOR STANDARDIZATION

The lowest water-vapour pressure which was to be measured was of the order of 0·1 mm. of mercury at atmospheric temperature. With such a low moisture-content the dew point is about −40° C. and consequently special apparatus had to be devised to reach these low temperatures.

The arrangement finally used is shown in figure 2. A copper rod about $\frac{1}{4}$ in. in diameter has a copper disc soldered on to it at one end. The lower end of the rod is flattened off on one side for about two inches and polished. This surface is then amalgamated with mercury to serve as the mirror for the detection of dew. A thermocouple is soldered into a hole drilled in the back of the rod so that the junction comes just behind the surface of the mirror. A line on the mirror-surface marks the position of the couple. A piece of brass tubing having a copper bottom soldered on to it serves as a container for a freezing-mixture of solid carbon dioxide and alcohol. The top of the disc on the copper rod and the bottom of the container are ground flat to ensure good thermal contact. A little alcohol placed on the surfaces prevents conductivity from being lowered by hoar frost.

In taking readings the freezing mixture vessel is placed on top of the mirror stem until dew appears, when the temperature is read by means of the thermocouple. It is then removed and the temperature at which the dew vanishes is noted also.

When the apparatus was first set up a mirror of highly polished stainless steel was used, but it was found that on continued exposure, sometimes at quite high temperatures, in the chamber containing concentrated sulphuric acid, its surface became dulled and the detection of the first traces of dew became correspondingly difficult. Since the steel mirror was very difficult to clean, mercury surfaces were tried and found to be quite satisfactory. These were prepared by polishing the surface with metal polish and then rubbing on a little mercury with the polish and

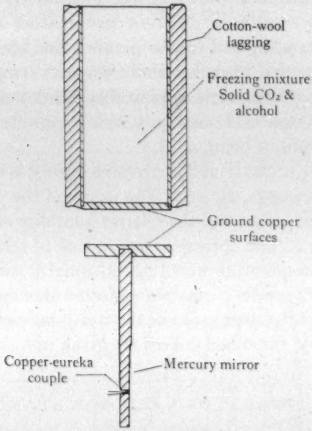

Figure 2. Dew-point apparatus for low temperatures.

finally cleaning with a dry cloth. Although the mirrors required fairly frequent renewal, this was so easy a task that they were used for nearly all the work described here. If the copper surface became badly pitted by mercury it was easily restored by buffing and a new mercury surface was applied.

At vapour pressures above that of water at 0° C., i.e. 4·58 mm. of mercury, the exact temperatures of appearance and disappearance of the dew were easy to determine. The mist could be watched as it crept down or up the mirror past the spot at which the thermocouple was fixed. Below this vapour pressure, however, the moisture appeared as hoar frost in tiny crystals almost all over the surface of the mirror at once. It was necessary to prevent the mirror from cooling too far past the dew point, or the temperature of disappearance would have been much too high owing to the poor thermal conduction between the frost and the mirror. This could be done by taking a preliminary run to estimate the approximate dew point and

then removing the freezing-mixture before this temperature was reached, so that the mirror only cooled down just as far as the dew point. When the mirror was cooled very slowly and closely watched, it was noticed that even at very low temperatures the whole surface of the mirror became misty just at the dew point, although this phase passed almost at once into the crystalline state. The best results were obtained when cooling was arrested just as the frost appeared in the misty stage.

To reach the very lowest dew-point temperatures necessary in this work, special care had to be taken to ensure fairly rapid cooling. It was found to be undesirable to lag the copper stem above the mirror on account of the moisture-retaining properties of the lagging. But by regrinding the copper surfaces from time to time and by taking care that a layer of oil did not collect on the bottom of the freezing vessel out of the carbon dioxide snow, it was possible to reach the lowest temperature necessary. Lower temperatures still could probably be obtained by increasing the diameter of the copper rod.

At the higher humidities the mirror was sometimes found to be cooling too quickly. The rate of cooling could be slowed up, however, by omitting the alcohol between the ground surfaces, or even by placing a thin sheet of paper between them. Alternatively, ice could be used in the pot instead of the usual freezing-mixture.

§ 4. THE WET-AND-DRY-THERMOCOUPLE APPARATUS

The chief difficulties arose from the very large depressions encountered at low humidities. At an air-temperature of 50° C. with a humidity of 1 per cent the depression of the wet junction was about 30° C., while at the highest air-temperatures used depressions of nearly 60° C. were encountered. With depressions of this order the conduction of heat to the junction along the wires, along the wick which wets it, and through the air becomes of importance, and unless special precautions are taken the depression for a given humidity and air-temperature will not be so great as that measured by the wet and dry thermometers.

Lanning[2] has described an apparatus in which wet and dry thermocouples are used for the measurement of humidity, and he encountered the same difficulty. He allowed for the difference by calibrating the apparatus for sulphuric acid solutions of known density. The aim of the present work has been to reduce the difference to a minimum so that the depression as measured by the thermocouples agrees with that measured by thermometers.

The final form of the wet-and-dry-thermocouple apparatus is shown in figure 3. The depression of the wet-junction temperature was measured by the two couples *A* and *B*, *A* being the dry couple and *B* the wet one. A copper eureka couple *C* serves to measure the air-temperature.

A wick for keeping the wet junction supplied with moisture could not be used, and the junction was wetted by allowing a single drop of distilled water to fall from a fine capillary tube on to a piece of cotton tied round the couple. To avoid excessive conduction along the wires, very fine wires, 0·0025 in. in diameter, of manganin and eureka were used, copper having too high a thermal conductivity. In order to ensure that the error due to wire conduction had been effectively eliminated, some

samples of exceedingly thin wire 0·0008 in. in diameter were tried. The depressions obtained were, however, identical with those obtained with the wires 0·0025 in. in diameter, and since the latter were much more robust they were used throughout. To keep the temperature of the dry junction steady at the mean air-temperature it was necessary to embed the wires in a fairly large globule of solder. The connexions to the potentiometer from the differential wet and dry couples were made from the

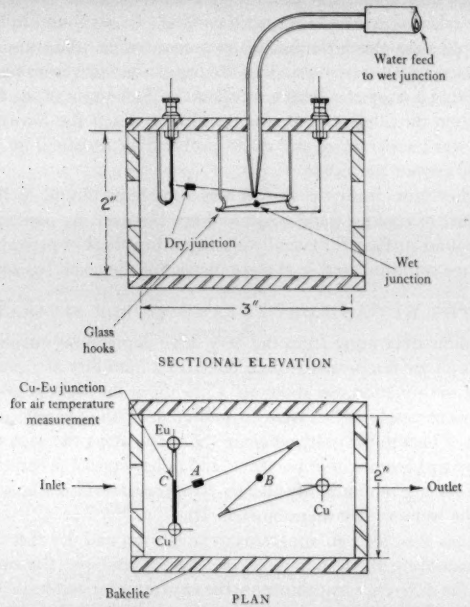

Figure 3. Arrangement of wet and dry thermocouples.

thin manganin wires to fairly thick copper leads to avoid any possibility of errors due to thermal e.m.fs. at these junctions, the thermal e.m.f. between copper and manganin being very small.

To avoid errors due to thermal conduction through the air it was found that the enclosure in which the couples were suspended must be of a certain minimum size. The necessary distance from the wet junction to the walls of the enclosure was determined by measuring the temperature-gradient through the air around the wet couple by means of a very fine exploring thermojunction. The temperature-gradient is shown in figure 4, from which it will be seen that the distance must be at least 1 cm. to ensure that the temperature-gradient shall not be disturbed by the presence of the walls of the enclosure.

With the apparatus assembled here it was found that the air-velocity past the couples necessary to obtain the maximum depression is very much less than that used in wet-and-dry-bulb thermometer measurements. This is in agreement with results obtained at the National Physical Laboratory[3] and by Hilpert[4]. Figure 5 shows the relation between depression and air-flow for a fixed humidity. With the

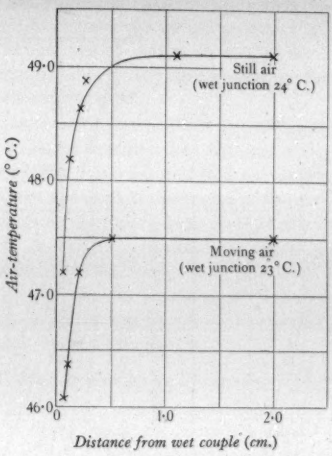

Figure 4. Temperature-gradient in air near wet thermocouple.

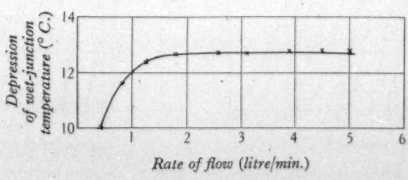

Figure 5. Effect of air flow on depression of wet thermocouple.

size of enclosure used, an air-flow of 3 litres per minute was equivalent to an air-velocity of about 2 cm./sec. This gives a great advantage over the wet-and-dry-bulb thermometer, which requires a minimum air-velocity of 3 m./sec., especially when small quantities of gas are being dealt with.

§ 5. DISCUSSION OF RESULTS

The final curves showing the relation between the depression of the wet-junction temperature and the humidity over the range of air-temperatures used are shown in figure 6. Between 30° C. and 80° C. the results obtained agree very closely with

those given by Griffiths. Above 80° C., however, the depressions given by the wet thermocouples are smaller than those obtained with thermometers. This is probably due to the fact that as the depressions become very large the error due to thermal conduction also increases. The results are plotted in figure 7 together with those of Griffiths. The curves below 30° C. are taken from the Smithsonian tables; they do not agree quite so closely with those obtained in the present work.

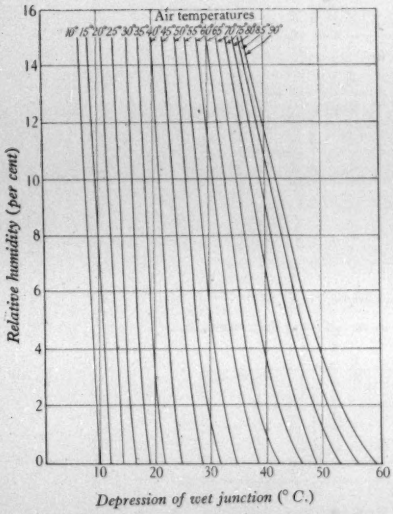

Figure 6. Relation between relative humidity and depression of wet-junction for air-temperatures from 10° C. to 90° C.

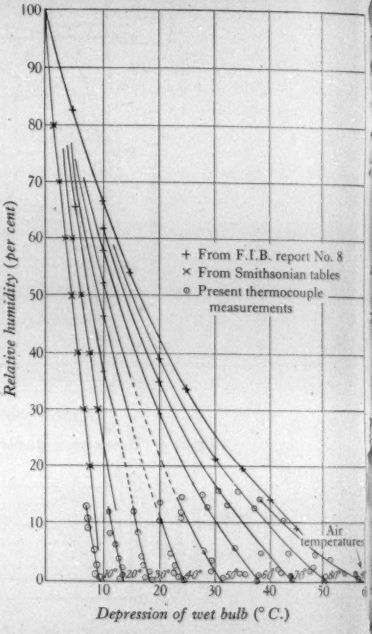
+ From F.I.B. report No. 8
× From Smithsonian tables
○ Present thermocouple measurements
Air temperatures
Relative humidity (per cent)
Depression of wet bulb (° C.)

Figure 7. Relation between relative humidity and depression of wet thermometer for various air-temperatures.

The usual formula for the wet-and-dry-bulb hygrometer has been applied to the results as follows:

$$p = pw - AP\,(t - tw),$$

where p is the pressure of water vapour in the air, pw the saturation vapour pressure of water at the temperature of the wet bulb, t the air-temperature, tw the temperature of the wet bulb, P the atmospheric pressure and A a constant. The value of A was found to be very nearly constant over the temperature-range from 10° C. to 70° C. and equal to 0·00072. From 70° C. to 90° C. the results were not in such close agreement, the value of A increasing for the higher vapour pressures.

A check on the accuracy of the calibrations was provided by the following experiment. The relative humidity of nitrogen from a cylinder was measured in three ways, (*a*) by absorbing the moisture in phosphorus pentoxide and weighing, (*b*) by the dew-point method, and (*c*) by the wet-and-dry-thermocouple apparatus.

The first time that this experiment was attempted the results did not show very good agreement, but this was found to be due to moisture which was given off by the rubber tubing used to connect the various pieces of apparatus to the nitrogen cylinder. When this rubber tubing was replaced by glass connected only by the shortest possible lengths of rubber, very close agreement between the results of the three different methods was obtained.

The weighing experiment was carried out by passing the gas very slowly over two drying tubes in series for several hours, the rate of flow being about 0·5 litre per minute. The rate of flow was measured by a previously calibrated flow-meter. No increase in weight was apparent in the second of the two drying-tubes, and this showed that complete absorption was taking place in the first.

A mercury-mirror dew-point apparatus was fitted up in a vessel so that a current of nitrogen could be passed through it. A pair of wet and dry thermocouples were also arranged so that the gas passed over them after passing through the dew-point instrument.

The results obtained were as follows:

Rate of flow of gas through phosphorus-pentoxide tubes	0·48 litre/min.
Duration of flow	4 hr. 48 min.
Increase in weight of first phosphorus-pentoxide tube ...	0·038 g.
Moisture-content of gas...	0·371 mg./litre.
Air-temperature	19° C.
Density of saturated vapour at 19° C.	16·4 mg./litre.
Relative humidity...	2·26 per cent.
Dew point	−27·3° C.
Air-temperature	19·0° C.
Vapour pressure	0·385 mm.
Saturation vapour pressure at 19° C.	16·5 mm.
Relative humidity...	2·33 per cent.
Depression of wet-junction temperature...	13·25° C.
Air-temperature	19·9° C.
Relative humidity from curves...	2·4 per cent.

Thus we have the following values for the relative humidity by three methods:

Chemical method	2·26 per cent.
Dew-point method...	2·33 per cent.
Wet-and-dry-thermocouple method	2·40 per cent.

The agreement between these results is sufficiently close for the work for which the apparatus was designed.

§ 6. ACKNOWLEDGMENTS

In conclusion, the author wishes to thank Messrs Callender's Cable and Construction Co. Ltd., in whose Wood Lane Laboratories this work was carried out, for permission to publish it, and Mr A. N. Arman, B.Sc., A.M.I.E.E., for much helpful advice.

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THE EFFECT OF PHASE-CHANGE ON THE COCHLEA

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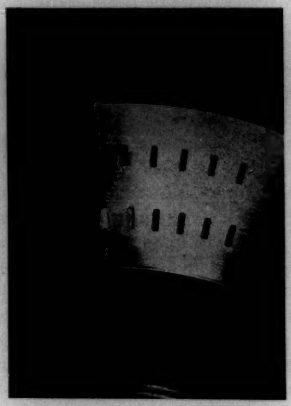
ABSTRACT. A change of phase in a siren tone is produced by means of a special spacing of the slots of the siren. A corresponding interruption of the tone is heard, in accordance with the resonance theory of audition.

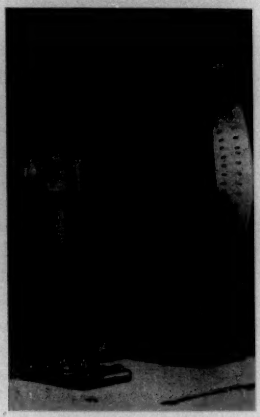
Some years ago I investigated the problem of introducing a sudden change of phase of π (half a wave-length) in a continuous single musical tone. A number of methods were tried without success, because either of noise, or of discontinuity of sound, or of both at the moment of phase-change. The method finally used was to rotate suddenly, through a few degrees, the wind chest of a de la Tour siren during the rotation of the siren disc. Each time this was done the intensity of the tone perceived by the ears was found to suffer a sudden interruption. This experiment is quoted by Beatty[1]. He adds "Békésy[2], however, repeated the experiment and was unable to detect any silent period". I thought it advisable therefore to repeat the original experiment in a different manner and this was done as follows. A brass disc about 12 inches in diameter was turned truly on a steel shaft. An inner circle of ninety-six equidistant slots was now milled through it from side to side, the distance between the first slot and the ninety-sixth slot being the same as the distance between any other two neighbouring slots. An outer circle of ninety-six equidistant slots was similarly milled through it, the distance between the first and the ninety-sixth slot being only half that between any of the other slots, so that a change of phase of π was thus introduced. When the disc is rotated by an electric motor, and a stream of compressed air through a slot-shaped jet is directed on to the inner circle of slots, a continuous musical tone of constant pitch is produced. When the stream of air is directed on to the outer circle of slots a musical tone of constant pitch is heard, but this tone is interrupted once at each revolution of the disc when the change of phase in the tone occurs. It was found further that the interruption detected by the ears can be imitated by stopping up two neighbouring slots of the inner circle. I concluded that the effect perceived by the ears was a true interruption and not, for example, a change of pitch of the tone. This experiment, therefore, confirmed in every respect my earlier experiment.

It was still possible, however, for the phase-change effect heard originally with the de la Tour siren and now similarly heard with the rotating disc to be due to changes taking place in some structure other than the cochlea of the observer.

Beatty, for example, suggested to me verbally that stationary waves at the walls and ceilings of the laboratory might explain the phenomenon, for when the siren disc is rotating and the musical tone is produced, some of the energy is used to set up and keep going the stationary wave pattern in the laboratory. When the phase is suddenly changed by π this stationary wave pattern would have to be abolished and would have to be replaced by an entirely fresh pattern. Powerful absorption of sound energy would therefore occur and this might be heard by the ear as a break in the sound.

Three experiments, in all of which the attempt has been made to eliminate the possible effects of sound-reflection by the room, have been performed: (i) The experiment has been done in the open air. (ii) The experiment has been repeated





in a sound-absorbing room. (iii) The sound has been conveyed to the ears from the slots in the rotating disc by means of a short length of thick-walled rubber tubing. The open-air experiment (i) was done on a flat asphalt roof far removed from other buildings. A strong wind was blowing. For experiment (ii) the sound-absorbing room was kindly put at my disposal by the General Electric Company. The following particulars of the room have been given me. It was 16 ft. long by 8 ft. high and 10 ft. wide, covered first with two layers of cabot quilt, and completely lined with seven layers of Camgee tissue. The absorption of low-frequency sound energy is believed to be due largely to the diaphragm action of the brown paper confining the eel grass of the cabot quilt, the paper being elastically supported but well damped on either side. In experiment (iii), the rubber pressure tube used was 13 mm. in outside diameter, 6 mm. in bore, and 11 in. in length. One ear was put directly to one end of this tube, the other end being close to the disc on the opposite side to the compressed-air jet.

In each case the effect perceived by the ear was an interruption in the musical note of the siren each time the change of phase occurred. Further it was found that a similar interruption could be produced by stopping up some neighbouring slots of the inner circle of slots which produced the continuous musical tone. The stopping of one slot produced an interruption that was rather less pronounced, while the stopping of two neighbouring slots produced an interruption that was rather more pronounced than that produced by the change of phase.

The resonance theory of the cochlea depends on two types of experiment for its support, (*a*) experiments showing that a definite place in the cochlea belongs to tones of a particular pitch and (*b*) experiments showing that there are resonators somewhere in the ear. With regard to the first type we may mention the recent experiment of Hallpike and Rawdon-Smith, who found that with low-pitched tones the voltage-fluctuations of the action currents were greater near the apex of the cochlea, whereas with high-pitched tones they were greater near its base. With regard to the second type of experiment, it is my opinion that the phase-change effect described in this paper comes in this category, because it is easy to explain the effect if there are resonators in the ear but difficult if there are not. The explanation on the resonator theory is as follows. On change of phase several effects occur: (1) The in-tune resonator comes to rest and then restarts in the new phase. This fall and rise in amplitude should cause an interruption in the tone to be heard. (2) The out-of-tune resonators on the high-frequency side accelerate after the phase-change until they match the new phase. (3) The out-of-tune resonators on the low-frequency side decelerate after the phase-change until they match the new phase. (4*a*) The resonator corresponding to the octave above the musical tone made by the siren receives a slight impulse if the phase-change has been produced by reducing by half the time interval between the positive phases. (4*b*) If, however, the phase-change has been produced by increasing by half the time interval between the positive phases, then it will be the resonator corresponding to the major fifth below the musical tone that will receive a slight impulse. (5) Most of the out-of-tune resonators vibrate with small amplitude for a short time after the phase has been changed. This should cause a noise to be heard and the noise should follow the interruption in the tone so closely that the two should be physiologically inseparable. We may say then that on the resonance theory an interruption accompanied by a noise should be perceived by the ears when the phase of a tone is changed by π.

The effect on the ear resonators of an actual interruption in a musical tone should be (1) a decrease in amplitude of the in-tune resonator, (2) temporary acceleration of the resonators just above in pitch, (3) temporary deceleration of those just below in pitch, and (4) transient swings of the out-of-tune resonators when the musical tone recommences. The physiological effect to be expected would therefore be a brief interruption in the musical tone accompanied by a noise due to the out-of-tune resonators. Therefore on the resonance theory we should expect a change of phase to produce the same sensation as a short interruption. The experiments described above show that such is the case.

There are many theories rival to that of resonance; one very widely held is the telephone theory. On this theory a change of phase should produce no other effect than the slight sounding of either the octave above or the major fifth below the musical tone suffering the phase-change. Since this is not the effect heard by the ear we conclude that the telephone theory fails to explain the observed phenomenon.

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DISCUSSION

Dr R. T. BEATTY. There is a formidable mass of anatomical and physical evidence that a frequency-analysis of sound takes place in the cochlea, so that there is a one-to-one relationship between pitch and position along the basilar membrane. Such localization of pitch is most plausibly explained by invoking the principles of resonance, and it is for this reason that the resonance theory, though seriously shaken in recent years, still maintains a strong position. The most direct evidence for resonance would be the demonstration of the existence of after-swings, and the author's experiments seem to give a direct proof of their existence.

We must, however, note that a contrary result has been obtained by Békésy,* who excited a telephone by an oscillatory circuit arranged so that by pressing a key the phase of the exciting current changed by 180°. No period of silence was observed. He then placed the telephone in a tuned circuit so as to increase the duration of the transient effect on the diaphragm and observed a silent period when the logarithmic decrement θ per cycle of the tuned system was 0·1. Hence he argues that if θ were equal to 0·1 in the ear resonators the silence should be observable, but as no silence is perceived $\theta \gg 0{\cdot}1$.

The author states that an interruption was noticed when one slot was closed. If we assume that a 10-per-cent decrease of amplitude of the ear resonator gives a perceptible effect, we have $0{\cdot}9 = e^{-\theta}$, or $\theta = 0{\cdot}1$, a value consistent with Békésy's result obtained with a tuned circuit. With this low value of damping we should anticipate a decided effect when the phase is reversed, and this has actually been obtained by Dr Hartridge.

The experiment is of great importance and it is to be hoped that the discrepancy between the work of the two authors will be cleared up.

AUTHOR'S reply. When I originally studied the phase-change effect in 1921 I found great difficulty in producing the phase-change without at the same time producing noises which masked in the ears the beat produced by the phase-change. One of the first methods to be tried was to connect head-phones to a 3-volt 50-cycle alternating current via a spring-actuated two-pole change-over switch which was connected in such a way as to produce a change of phase of half a cycle on release

* *Phys. Z.* **29**, 799 (1928).

of the spring. The spring-release was found to be accompanied by a loud click in the telephones which entirely masked any phase-change effect, and this click was reduced but not eliminated by earthing the wire connecting the two magnet bobbins of the telephones. The click is probably due to sudden changes of potential at the telephones, for when the switch contacts break there is a sudden drop in potential, the magnitude of which depends on the point of the cycle at which the break occurs; and when the switch contacts close again there is a sudden rise in potential the magnitude of which depends on the point of the cycle at which closure occurs. Now by chance either breaking or making circuit might coincide with one of the zero-potential points of the a.-c. cycle but it is extremely unlikely that both would do so, and therefore the click is unavoidable and the method a useless one in my hands. I therefore tried other methods of changing phase until finally the de la Tour siren was found to give satisfactory results.* With these unsatisfactory results obtained with head-phones fresh in my memory I am not surprised that Békésy failed. I should indeed have been very surprised if he had succeeded.

Mr C. N. Smyth. The author has demonstrated a very interesting experiment, which if sufficiently rigorous will do much to confirm the resonance theory. I feel however that a careful examination needs to be made before it is accepted as conclusive evidence.

The proof of the theory lies in the nature of the silent period to be noticed during the sudden change of phase. Is the short click heard really a silent period, or the production of harmonics external to the ear at the sudden interruption of the note?

To decide this point, electrical methods, and filters, are not conclusive enough, owing in part to the finite mass of the sound-producing mechanisms employed. Would it not, however, be possible to use a siren note of the order of 12,000 c./sec., so that all harmonics would fall outside the audible range? This should be possible with an 8-in. disc and a speed of 3000 r.p.m.; or the services of a top-note deaf observer might reduce the mechanical difficulties. Should the effect not then be noticeable, the magnitude could be increased by having a large number of reversals for every rotation of the siren wheel and listening, under carefully controlled conditions in a damped chamber, for a change in the loudness of the note.

Author's reply. The beat ought theoretically to consist of a short silence plus a short noise. Observation appears to confirm this. It is quite possible that to some observers the silence, and to other observers the noise, appears to be the prominent feature. If the disc be rotated at fast speeds (e.g. 50 revolutions per second) the beat is still there, but at very fast speeds (say 100 rev./sec. or more) its perception fails, possibly because of the short times intervening between repetitions. This difficulty could be avoided by using a siren with a greater number of slots. The present disc is 30 cm. in diameter with 96 slots. If the number were doubled,

* *Brit. J. Psychol.* **12**, 142 (1921).

the spacing being the same, the disc would have to be 60 cm. in diameter. The cost of this would be well-nigh prohibitive. If sound film were used it would have to pass the photocell at a speed of about 100 or 200 feet per second. If a gramophone disc were used its speed of rotation would have to be approximately 30–60 rev./sec., so that in each case difficulties, not by any means insurmountable, may be anticipated in attempting to get a tone of 12,000 c./sec.

Dr W. S. STILES. The author has used the term "period of silence" in describing the phase-change effect. I have not had an opportunity of hearing the effect before, and my first impression is of a metallic rap on a background of musical note, with no easily perceptible silent period. In the comparison experiment, which closely simulates the phase-change effect when one or two slots are stopped, it is possible to lengthen the silent period by stopping more slots. I should like to ask the author if there is any marked change in the character of the effect observed as the number of stopped slots is increased.

AUTHOR's reply. The phase-change causes effects at the ear which closely resemble those produced by a brief interruption in a continuous tone: a silence plus a noise. The cause of the noise has already been elucidated.* A longer interruption produces a relatively larger silence effect and a relatively smaller noise effect.

Mr L. V. K. REIN asked whether the author had given any consideration to the question of bone conduction in connexion with the experiment.

AUTHOR's reply. The possible effects of bone conduction have been carefully considered. Since the phase-change beat is heard when the sound is led from the siren by a rubber tube to one ear only, the other ear being plugged, and since Banister found that bone conduction *of sound* (in contradistinction to bone conduction of changes of electric potential) is negligible in man, I think it is safe to assume that the phase-change beat does not depend on bone conduction.

Mr J. H. SHANBY. I hope that the author will be able to join forces with Hallpike and Rawdon-Smith at the Middlesex Hospital, present his phase-changed and interrupted sounds at the cat's ear, and observe the results both in the potentials produced on the loud-speaker and after the sounds have been passed through the cat's auditory machinery.

AUTHOR's reply. Arrangements have already been made for carrying out this suggestion. With Dr Hallpike's and Dr Rawdon-Smith's assistance the wave-form of the siren has been photographed. With a narrow high-velocity jet it is found to be very peaky. With an 8-mm. jet the wave is found to be somewhat flat-topped. With a 5-mm. jet, or better an oval jet measuring 4 mm. × 6 mm., with its long axis parallel to the long axis of the slots, a very fair sine wave is obtained. When tested on the ear the phase effect is still there and presumably the presence of harmonics is therefore not necessary for the phenomenon.

* Hartridge, *Brit. J. Psychol.* **11**, 277 (1921).

Dr J. E. R. CONSTABLE. The fundamental importance of the author's very interesting experiment justifies further attempts to obtain more conclusive results. For instance, an oscillographic study of the note emitted should be made to establish that the short hiss which formed the interruption is not present in the note emitted from the siren. It could, for example, be argued that, as is shown by the photograph of the siren disc, the two phase-changing slots are so near together that there is a position in which air from the jet can pass simultaneously through both. This would produce a short hiss once during each revolution, just as was observed. A test of this explanation could be quickly made by milling a slot midway between two of the slots in the inner circle of equally spaced slots. This, without introducing a phase-change, would make it possible for the air to pass through two slots at once. If the periodic interruption did not then appear, one could feel more sure that the phenomenon was of subjective origin.

If an independent method of producing the phenomenon could be devised it would be of very great value. The author has naturally already tried a number of methods. He mentioned, in particular, that electrical methods are unsatisfactory owing to the clicks caused by switching. There is an additional difficulty about electrical and, indeed, many other methods, namely the fact that they must necessarily involve vibrating systems such as the diaphragm of a telephone receiver. Thus if any phenomena which occur when these methods are used could be accounted for by resonators in the ear they could also be accounted for by the resonant system used for producing the sound. The ambiguity which thus arises could only be dealt with by making measurements of the duration of the interruption.

The possibility of using an electrical method of investigating the phenomena is therefore dependent upon the possibility of designing an electro-acoustic system the phase of which can be reversed in a time which is distinguishably shorter than the two or three periods apparently required by the ear resonators. This requirement would be fulfilled by an aperiodic electro-acoustic system. To be sure of the result, however, it would be necessary to have a more accurate method of estimating the length of the interruption.

The author's observation of the time taken to reverse the phases of the ear resonators also affords a rough method of calculating their sharpness of tuning. The reversal of the phase of the driving force would cause the response of the resonator to fall at first to a minimum value and then to increase again. It would, strictly, take an infinite time to reach its previous amplitude. However, the increase is rapid at the beginning, so that effectively the response returns to its original value in a time which is much the same as that taken for it to reach its minimum. We may take it therefore that the time taken for the response to reach its minimum is of the order of one period of the note. Calculations made on this basis show that the sharpness of tuning of the ear resonators is about 24; i.e. for a note of 500 c./sec. a mistuning of 20 c./sec. would produce a fall in the response of about 3 decibels.

AUTHOR's reply. With the aid of Dr Hallpike and Dr Rawdon-Smith a cathode-

ray oscillograph record of the note emitted has recently been obtained. With a suitable jet of oval or round section, contrary to expectation, a very fair sine wave-form can be obtained. There is of course some hiss from the siren but it does not appear to affect to any obvious extent the crystal microphone used. I think Dr Constable's point about air passing simultaneously through two jets is met by two variations of the normal procedure: (i) If we use a very small pointed nozzle giving a narrow high-velocity jet of air and place this close to the siren disc the passage of air simultaneously through two neighbouring slots seems very unlikely and yet the phase effect is heard in the normal manner. (ii) The phase can be changed not only by reducing by half a wave-length the distance between groups of slots but also by increasing the distance by half a wave-length. When the latter is done the probability of air passing through neighbouring slots is greatly decreased and yet the phase effect heard by the ear appears to be quite normal. With regard to an independent method of producing the phenomenon I am proposing to try a sound-film record of a tone of constant pitch with the phase-change produced both by cutting a half-wave-length piece out and by putting a half-wave-length piece in. For loud-speaker I propose to use the Duddell sound-producing arc since this is free from diaphragm resonances. When this apparatus has been satisfactorily set up I will ask Dr Constable to come and listen to the resulting phase-change.

If this method proves difficult there is a gramophone-disc method which may be tried as an alternative.

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THE DEPENDENCE OF SENSITIVITY OF THE SELENIUM-SULPHUR RECTIFIER PHOTO-ELECTRIC CELL ON THE OBLIQUITY OF THE INCIDENT LIGHT, AND A METHOD OF COMPENSATION THEREFOR

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ABSTRACT. The paper describes an investigation of the loss of sensitivity of the selenium-sulphur rectifier photoelectric cell with increasing obliquity of the incident light. When a restricted portion only of the surface of the cell is illuminated, it is found that the sensitivity increases as the centroid of the illuminated area is displaced from the centre of the cell. This permits of a simple method of compensation for the fall in sensitivity at oblique incidence, comprising the use of a central stop arranged at a suitable distance above the surface of the cell.

§1. INTRODUCTION

The rectifier photocell can be successfully employed for precise work in illumination photometry only when its sensitivity, defined as the short-circuit current per unit of luminous flux, is independent of the obliquity of the incident light. In any actual cell there is usually a serious loss of sensitivity when the angle of incidence exceeds 70°.

This loss of sensitivity has been observed for many types of marketed cells, and several authors[1,2,3] have suggested possible methods of compensation. Measurements showing the dependence of the sensitivity for normal incidence upon the position of the centroid of the illuminated area when a restricted portion only of the surface of the cell is illuminated are here described; they prove that the sensitivity increases as the centroid of the illuminated area is displaced from the centre of the cell. This result permits of a method of compensation for the fall in sensitivity at oblique incidence, comprising the use of a central stop in front of the cell.

§2. DETAILS OF APPARATUS AND SPECIFICATION OF MEASUREMENT

Cells of the type designated "class A" in an earlier paper[4] were used for the experimental work. The cell under test was mounted in a holder *AB*, figure 1, and illuminated by a 100-V. 250-W. projector lamp *L*. The lamp was fixed on an arm *c* so that it could be moved round the circumference of a semicircle of radius 100 cm.,

whose centre O coincided with the centre of surface of the cell. When c was normal to AB, the perpendicular to AB through O passed through the light-centre of the lamp, the plane of the filament being parallel to the plane of AB. A telescope was used in the adjustment of the lamp filament. The dimensions of the filament were such that at a distance of 100 cm. the lamp could with sufficient accuracy be re-

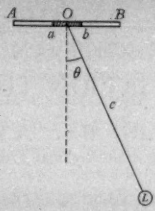

Figure 1. Diagrammatic representation of disposition of apparatus for measuring the distribution curve of sensitivity of a rectifier photocell.

garded as a point source. Moreover, since the maximum radius of the circular plane surfaces mounted in the holder was only 2·5 cm., and therefore small in comparison with the distance of the source, the illumination could be considered to be sufficiently uniform over the surface for the cosine law to apply.

The lamp was operated at 90 volts and gave a candle-power of 282 candles at a colour temperature of 2765° K.; the maximum illumination produced at the cell was, therefore, 282 metre-candles or 26·2 foot-candles. For the range 0 to 26·2 ft.-can. the following relation[4] holds between short-circuit current, i_e, and illumination E,

i_e, E

$$i_e = aE - bE^2 \qquad \text{.....(1)},$$

a, b, I, d where a and b are constants. If I denotes the candle-power of the source, and d the radius of the semicircle, the illumination E at the surface of the cell for any angle

θ of incidence, θ, is given by

$$E = (I \cos\theta)/d^2.$$

Thus if the sensitivity is assumed to be independent of the obliquity of the incident

i_0 light, equation (1) will give for the short-circuit current i_0 at normal incidence:

$$i_0 = \frac{aI}{d^2}\left\{1 - \frac{b}{a}\cdot\frac{I}{d^2}\right\};$$

i_θ and at any other angle of incidence θ the short-circuit current i_θ will be given by

$$i_\theta = \frac{aI\cos\theta}{d^2}\left\{1 - \frac{b}{a}\cdot\frac{I\cos\theta}{d^2}\right\}.$$

Since terms involving higher powers of the quotient b/a may with sufficient accuracy be neglected, these equations combine to give

$$\frac{i_\theta}{\cos\theta} = i_0\left\{1 + \frac{b}{a}\cdot\frac{I}{d^2}(1 - \cos\theta)\right\}.$$

In an actual cell the sensitivity is a function $f(\theta)$ of the obliquity of the incident light, so that we may write $f(\theta)$

$$\frac{i_\theta/\cos\theta}{i_0\left\{1+\frac{b}{a}\cdot\frac{I}{d^2}(1-\cos\theta)\right\}}=f(\theta) \qquad \text{.....(2).}$$

The curve represented by this equation will be referred to as the *distribution curve* of sensitivity of the cell. The curves given in all the figures are mean-distribution curves for two coplanar quadrants.

§ 3. UNCORRECTED DISTRIBUTION CURVES

Selenium is extremely hygroscopic, and adequate steps must therefore be taken to avoid exposing the selenium-sulphur film to moist air. Also exposure of the sputtered metal to the atmosphere is found to result ultimately in its complete

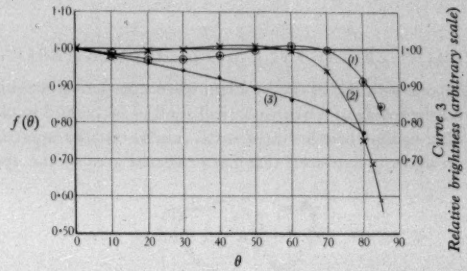

Figure 2. Distribution curves of sensitivity (1) for unlacquered cell and (2) for lacquered cell; and distribution curve (3) of brightness for depolished opal surface with normal view.

disintegration, metallic aggregates gradually forming and giving rise to electrical discontinuities. A normally sensitive cell may after two months' exposure become almost completely insensitive to light; the cell cannot then be restored to its previous sensitive state.

The cell may be hermetically sealed with a glass window; this method is used in the Weston Photronic cell. It leads, as is shown by the work of Goodwin [1], to an increasingly serious loss of sensitivity with increase in the obliquity of the incident light, owing to loss of light by reflection from the glass window. Alternatively, the cell may be coated with a colourless moisture-proof permanent lacquer; this method has been adopted for the cells produced at the National Physical Laboratory. A lacquer made by the Research Association of British Paint, Colour and Varnish Manufacturers has proved to be satisfactory; it contains cellulose, low-viscosity vinyl acetate, and barkite.

Figure 2 gives distribution curves (1) for an unlacquered cell and (2) for the same cell lacquered. It also gives the brightness-distribution curve (3) for normal view for a ground opal glass test-surface such as is usually employed with a visual

illuminometer. In the case of the unlacquered cell, curve (1), it is seen that the departure from the cosine law is, at any angle of incidence up to 85°, less than that for the depolished opal surface, curve (3); on the other hand, when $\theta > 80°$ the divergence for the lacquered cell, curve (2), becomes increasingly greater than that for the opal. Without correction the lacquered cell cannot be regarded as a satisfactory photoelectric substitute for a visual photometer.

The fall in sensitivity with increasing obliquity of the light may result from (i) loss of light by specular reflection, (ii) dependence of the velocity-distribution of the photoelectrons upon the angle of incidence, or (iii) change in the state of polarization of the light after the light has entered the selenium-sulphur film, giving rise to a change, dependent upon the angle of incidence, in the directional distribution of the liberated electrons. In the case of the lacquered cell, curve (2) shows that much of this decrease in sensitivity is attributable to loss of light by specular reflection. Methods of compensating for this fall in sensitivity will now be considered.

§4. HEMISPHERICAL CELL WITH CIRCULAR APERTURE

At first sight one solution of the problem of compensation would appear to be to form a cell on the inside of a hemispherical shell of metal and to close the hemisphere with a thin opaque disc having a small central circular aperture. From the design shown in figure 3 it is seen that the projected area of the aperture on the

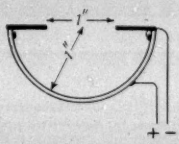

Figure 3. Hemispherical cell with central circular aperture.

surface of the cell is proportional to the cosine of the angle θ between the normal to the plane of the aperture through its centre and the direction of the incident light; hence the incident light-flux is proportional to $\cos\theta$. Further, with the dimensions given in figure 3, light is incident on the hemispherical surface of the cell at an angle not exceeding 30°. Several hemispherical cells were constructed according to this design.

A number of difficulties are involved in the construction of such cells; it is necessary here to mention only two. It is essential first to obtain on the inside of the hemispherical shell a thin and uniform coating of the selenium-sulphur mixture, and for this purpose a polished steel ball very slightly less than two inches in diameter has been used. After annealing, the hemispherical selenium-sulphur film has to be sputtered, and here again the difficulty is to secure a uniform coating. The non-uniform electrostatic field created by the presence of the hemisphere necessitated a modified electrode arrangement, the success of which in producing uniformity of sputtering was confirmed by further results obtained with cells in which

a graphite film replaced the sputtered metal film. Uniform and continuous graphite films were obtained by careful polishing with finely powdered Acheson's graphite. A circular Wood's-metal ring around the top of the hemisphere served to make contact with the metal or the graphite film.

The distribution curve given in figure 4 is representative of the results obtained. There is a discontinuity in the curve when $\theta = 52{\cdot}5°$, since with further increase in θ the illuminated area on the hemispherical surface increasingly overlaps the ring electrode, so that the response falls off.

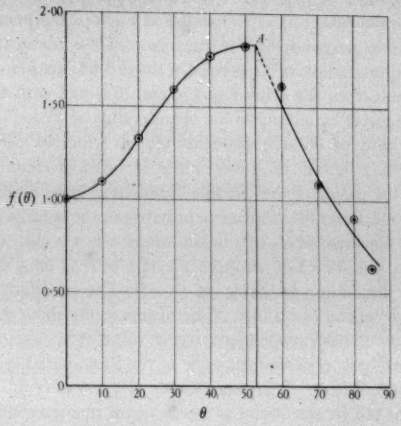

Figure 4. Distribution curve of sensitivity for hemispherical cell with central circular aperture.

The more important part of the curve is that from $\theta = 0$ to $\theta = 52{\cdot}5°$. It will be shown below that the increase of sensitivity with θ in this region is a consequence of the dependence of the sensitivity upon the position of the centroid of the illuminated area with respect to the circular collecting electrode. This effect renders the hemispherical cell quite useless for the purpose for which it was originally designed.

§ 5. DEPENDENCE OF SENSITIVITY UPON THE AREA OF ILLUMINATION AND UPON THE POSITION OF ITS CENTROID: DISC CELLS

The work on the hemispherical cell indicated that the sensitivity depended either upon the area of illumination, or upon the position of the centroid of the illuminated area with respect to the ring electrode, or upon both. Accordingly, a further investigation of the disc cell was made, and three experiments were carried out. These were confined to circular illuminated areas with light incident normally.

§ 6. DETAILS OF APPARATUS AND EXPERIMENTAL WORK

A holder for an adjustable iris diaphragm was constructed so that it could be mounted vertically on a three-metre photometer bench. The cell under test was mounted on a teak panel which could be easily and accurately moved in a plane parallel with the plane of the diaphragm and 1 cm. behind it. The height of the cell was adjusted so that with a normal view its centre appeared to move along a diameter of the circular aperture. A 1000-W. 100-V. gas-filled projection lamp, operated at 50 V., to give a candle-power of 216·5 candles at a colour temperature of 2360° K., in a known direction perpendicular to the plane of the filament, was set on the bench so that the illumination at the surface of the cell was 10·4 ft.-can., the distance of the lamp filament from the cell being 139 cm. Contact with the sputtered film of the cell was secured by means of an opaque ring of Wood's metal, of inside diameter 3·8 cm. and of outside diameter 4·2 cm., melted centrally on to the selenium-sulphur film before the sputtering to serve as an electrode of the cell.

r_1, r_2 Let r_1 denote the radius of the circular illuminated area, r_2 the inside radius of
t the circular electrode, and t the displacement between the centres of the two circles.

Experiment 1. Various values of t in the range 0 to 1·2 cm. were taken, and at each value of t, r_1 was increased through a range of 0·35 cm., the smallest value possible with the diaphragm available, to (r_2-t). The sensitivity of the cell was determined at each setting of t and r_1. The observations show that the sensitivity for any given value of t is independent of the value of r_1, i.e. of the area of the circular illuminated spot, provided the edge of the illuminated area is not too close to the ring electrode. When r_1 is increased from $(1{\cdot}7-t)$ to $(1{\cdot}9-t)$, r_2 being equal to 1·9 cm., a slight fall in sensitivity is observed up to a maximum of 5 per cent; but the results obtained for this region are not very consistent. We have therefore the following general empirical result: When the centroid of the illuminated area is fixed, the sensitivity is, for circular illuminated areas, independent of the area of illumination, so long as the edge of the illuminated spot is not very close to the circular electrode.

Experiment 2. With r_1 fixed at 0·35 cm., values of t in the range 0 to 1·2 cm. were taken. At each value of t the illumination at the cell was varied over the range 0 to 17 ft.-can. A curve relating short-circuit current with illumination was thus obtained for each value of t. The observations showed that the deviation from true proportionality between short-circuit current and illumination was the same to within ± 2 per cent for all curves, and therefore that the constants a and b (of equation (1)) are independent of the part of the cell-surface illuminated.

Experiment 3. The lamp was set so that the illumination at the surface of the cell was 10·4 ft.-can., and the following values of r_1 were taken: 0·375, 0·45, 0·55, 0·65 and 0·75 cm. At each value of r_1, t was varied through the range 0 to r_2-r_1, and the sensitivity was determined for all values of t. The results are plotted in figure 5, which gives the curves relating sensitivity with t for the various values of r_1. It is seen that the sensitivity is markedly dependent upon the position of the illumi-

nated spot with respect to the electrode: the sensitivity increases as the edge of the illuminated area approaches the electrode.

The increase of sensitivity with displacement of the illuminated spot towards the ring electrode is doubtless due to the fall in electric resistance of the path of the electron-current from the illuminated area to the ring electrode along the homogeneous and uniform sputtered film.

With the smallest value of r_1, t was increased beyond r_2-r_1; the illuminated area of the selenium-sulphur surface was thereby reduced, since the illuminated spot overlapped the metal ring to an extent given by the formula

$$A=r_1^2\cos^{-1}\left(\frac{r_2^2-r_1^2-t^2}{2r_1t}\right)-r_2^2\cos^{-1}\left(\frac{r_2^2-r_1^2+t^2}{2r_2t}\right)$$
$$+t\sqrt{\left\{r_1^2-\left(\frac{r_2^2-r_1^2-t^2}{2t}\right)^2\right\}} \quad \ldots\ldots(3).$$

Since the incident light-flux is considered to be constant, the apparent sensitivity is reduced in the ratio of the effective area to the total area of illumination. This is shown for the case where $r_1=0{\cdot}375$ cm. in figure 5.

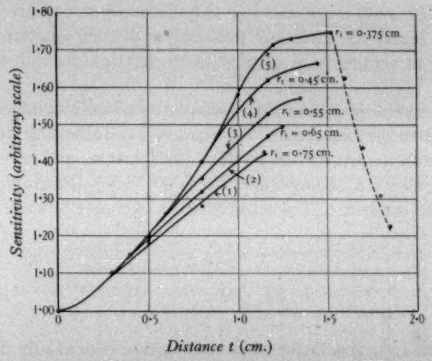

Figure 5. Curve showing the dependence of sensitivity upon the position of the centroid of the circular illuminated spot for various values of r_1.

The observations made in this experiment give the following general empirical result: When a restricted area only of the surface is illuminated, the sensitivity depends upon the position of the centroid of this area, increasing with the displacement of the centroid from the centre towards the periphery of the cell.

§ 7. DISTRIBUTION CURVES FOR DISC CELLS PROVIDED WITH CENTRAL STOPS

It is seen from figure 5 that advantage may be taken of the increase of sensitivity with t in order to compensate for the loss in sensitivity of the disc cell with increasing obliquity of the incident light, by providing an aperture of suitable radius fixed

centrally at a suitable distance above the surface of the cell. Measurements have been made, with steel and aluminium apertures of various radii, on a number of cells. Representative results are plotted in figures 6 and 7. The correct position of the aperture was determined when the perpendicular to the surface of the cell through its electrical centre passed through the centre of the aperture. The electrical centre was usually at the geometrical centre, but in some cases it appeared to be slightly displaced. At the inside edge of the aperture the thickness of the metal diaphragm was usually made about 0·3 mm. The distance of the aperture from the surface of the cell was measured with a micrometer depth gauge. In figures 6 and 7 the line *C* marks the angle of the incident light at which the edge of the illuminated spot reaches the collecting ring; further increase in obliquity beyond *C* would, of course, result in a large decrease in apparent sensitivity.

With an aperture of radius 0·75 cm., at a distance of 0·75 mm. from the surface of the cell, the deviation of $f(\theta)$, equation (2), from unity is not greater than ± 3 per cent for any value of θ from 0 to 85°, figure 7; with the same aperture at a distance of 0·70 mm. the divergence is not greater than ± 5 per cent for any value of θ from 0 to 87°. These results hold to within ± 2 per cent over a range of illumination of 0 to 25 ft.-can. at normal incidence. It is only necessary to compare figures 6 and 7 with figure 2 to realize the success of this method of compensation in neutralizing the falling away of sensitivity of rectifier photoelectric cells with obliquity of the incident light.

The use of a central stop naturally involves a considerable reduction in the total short-circuit current per foot-candle. For example, a cell of sensitivity 260μA./lumen gives approximately 3·5μA./ft.-can. without the aperture, and only about 0·5μA./ft.-can. with the aperture. A larger aperture is not very satisfactory, as is shown by the results plotted in figure 6. The sensitivity can of course be increased by making larger cells.

§ 8. DISTRIBUTION CURVES FOR DISC CELLS PROVIDED WITH CENTRAL STOPS: COLOURED LIGHT

If the specular reflection factor of the cell-surface is markedly dependent upon the wave-length of the incident light, the distribution curve given in figure 7, curve (2), will only apply for light of colour temperature 2765° K. Actually, however, Pfund[5] showed that the maximum variation of the reflection factor of an annealed selenium plate throughout the wave-length range 4500 to 7000 A. was only about 15 per cent of its minimum value. In consequence no very considerable change in the distribution curve is to be expected in the usual range of colour temperature encountered in photometry.

In order to examine this, a holder to carry a standard colour filter was fixed near and in front of the lamp *L* on the arm *c*, figure 1. The lamp was operated at 96 V. at a colour temperature of 2830° K., and a central stop of radius 0·75 cm. was fixed at a distance of 0·75 mm. from the surface of the cell. The distribution curve was then determined for white light. A colour filter was inserted in the holder, and the

distribution curve redetermined. Distribution curves were obtained with the following colour filters: light green, ortho green, daylight, light orange and light red.

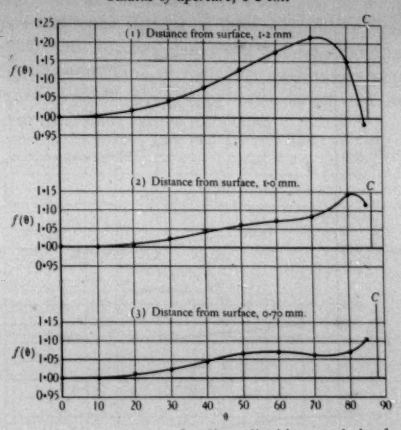

Figure 6. Distribution curves for disc cell with central circular stop.

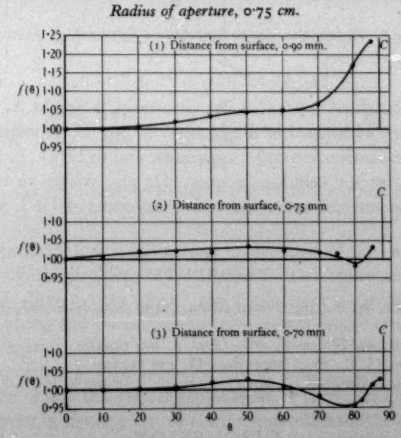

Figure 7. Distribution curves for disc cell with central circular stop.

The quotient of $f(\theta)_c$ for coloured light and $f(\theta)$ for white light is plotted against θ for each filter in figure 8. The results are sufficient to show that with the usual colour-

differences encountered in illumination photometry, the departures from the distribution curve given in figure 7, curve (2), are unlikely to be greater than ± 10 per cent, and in most cases would be much less than this.

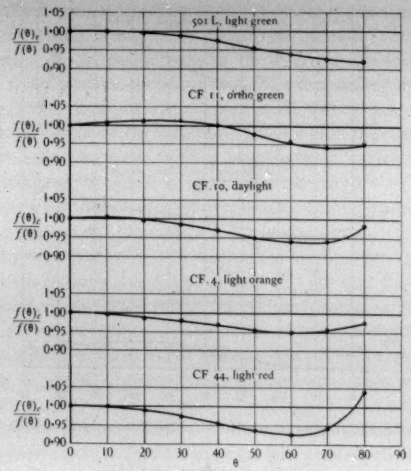

Figure 8. Distribution curves for coloured light: $f(\theta)_c/f(\theta)$ versus θ.

§ 9. ACKNOWLEDGMENTS

The author is indebted to Mr C. J. W. Grieveson, B.Sc., M.A., for his assistance in the experiments with the iris diaphragm; to Mr C. Dunbar, M.Sc., for his assistance with the distribution curve apparatus; and to Dr G. F. New, of the Paint Research Station, for the cellulose lacquer. He also wishes to record his sincere thanks for the kind interest and constructive criticisms of Dr J. W. T. Walsh and Dr D. Owen.

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DISCUSSION

Prof. L. C. Martin asked the author to give particulars of the colour filters used by him.

Dr O. Owen asked whether results such as those expressed in figure 5 were deducible from any theories of the rectifier cell.

Dr W. D. WRIGHT enquired whether the characteristics shown in figure 5 varied from cell to cell or were common to all cells of a given type.

AUTHOR'S reply. The details desired by Prof. Martin are given in figure 9, which gives the spectral transmissions of the colour filters from 4000 to 7500 A. From these curves, the spectro-photoelectrical sensitivity curve[4], and the spectral-energy distribution curve of the tungsten-filament source operating at a colour temperature of 2830° K., the effective wave-length and the effective integral transmission ratio of each filter can be calculated.

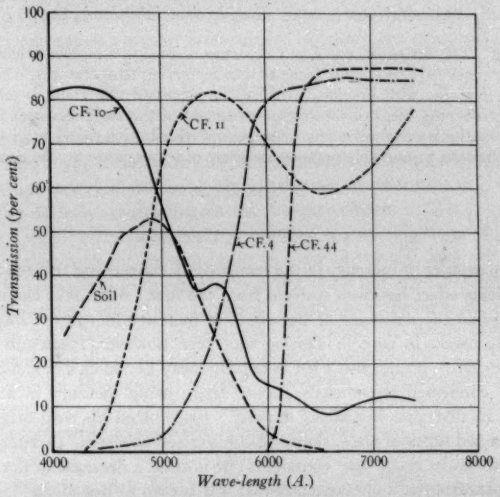

Figure 9. Spectral transmissions of colour filters used to obtain distribution curves for coloured light, figure 8.

I have attempted to find a theoretical explanation of the shape of the curves in figure 5. Strictly, the problem cannot be considered simply as one of conduction in two dimensions. Again, only when t, the displacement, is zero is the distribution of electron-flow along the homogeneous and uniform sputtered film radial. The theoretical investigation is not yet complete, but at present it appears that the available data necessitate a number of simplifying assumptions which would render doubtful the value of any theoretical explanation. I thank Dr Owen for his query.

The curves given in figure 5 are, of course, only valid for the cells described in a previous paper[4]. For cells of the type designated class *A* in that paper, experience has shown that the results hold to within 2–3 per cent.

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THE LONGITUDINAL THERMOELECTRIC EFFECT: (6) MERCURY

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ABSTRACT. The Benedicks e.m.f. in mercury contained in an unconstricted glass tube is observed to undergo a reversible decrease with increasing temperatures. The result is in qualitative agreement with previous work. It is suggested that there is an anisotropic quasicrystalline arrangement of the surface molecules of the mercury depending on temperature. Quantitative analysis of the temperature distribution failed to give the homogeneous coefficients, presumably because the effect of temperature on the constants is too marked.

§ 1. INTRODUCTION

The importance of mercury in the controversy concerning the existence of the Benedicks effect has been realized from the first. Benedicks claimed to have established the existence of the effect in mercury in 1917[1] and published corroborative results in 1919[2]. During that year, however, Haga and Zernicke[3] announced negative results and tried to explain away Benedick's evidence. In 1920 Gouineau[4] confirmed Benedicks's results again, using mercury in a constricted glass tube. In that year Benedicks himself[5] reproduced his own original results using constricted tubes of glass, slate and compressed asbestos. In 1921 Bernade[6] also obtained results using slate containers; he noticed a decrease of the effect with increasing temperature, a phenomenon that was known to Benedicks[2], and he was led by this to explain the e.m.f. as due to surface effects between the mercury and the slate container.

The most recent work by Tsutsui[7] avoids the constricted tube, and immerses the mercury in a uniform capillary glass tube. Tsutsui verified previous positive results, in general, but concluded that the e.m.f. must be due to a molecular or ionic layer constituting the interface between the mercury and glass.

In view of the lack of conclusive agreement, it was thought worth while to check the results for mercury again in the light of methods developed and results obtained here in connexion with other metals.

§ 2. EXPERIMENTAL METHOD

The heating-system was the same as that used in work on silver[8] to produce asymmetrical temperature-distributions. The mercury was contained in the same glass tube that was used previously to insulate the silver specimen from the brass

thermal shield. Outside the heating-system the glass tube was connected with flexible rubber tubes consisting of bicycle valve tubing; these carried the mercury down to the thermostat where junction with the copper leads was effected. To insure a complete circuit within the mercury a T piece was inserted near the heating-system and the mercury-level in this was kept above that in the heater. This open end also served to take up the mercury forced from the heater by thermal expansion during tests.

No satisfactory method could be devised of getting a map of the temperature-distribution in the mercury. All that could be said was that for the same heating-current that was used formerly, the temperature-distribution would be roughly similar with that obtained for wires passing through the glass tube. Since however the mercury represents a greater cross-section of good conducting material than was present in the case of a wire specimen, the temperature-gradients would certainly be less steep. This means that no good analysis of the e.m.f. is possible from the point of view of the theory used in previous papers. It is also difficult to see how we could improve this situation, even by inserting a travelling thermocouple in the body of the mercury: even if the mere mechanical difficulties in the way of such a device were overcome it would still be doubtful whether the thermo-e.m.f. of the couple could be successfully insulated from the mercury circuit.

To get a rough estimate, the effect was tried of inserting wires of greater cross-section, together with the thermocouple in place of the mercury. It was found to decrease the maximum temperature by a few units per cent. We estimate that at least an approximate idea of the maximum temperature can be found for the case of mercury by subtracting 10 per cent from the values previously found for corresponding values of the heating-current. Had the values of the e.m.f. given promise of better analysis, this method of approximation to the temperatures would have been pursued in greater detail. The e.m.f. was measured by the Paschen galvanometer as before, with its sensitivity at 0·094μV./cm.

§ 3. RESULTS AND DISCUSSION

In the following table the e.m.f. is recorded against the approximate maximum temperature found as mentioned above. In each case the temperature of the water bath, which was at the lowest point of the temperature-distribution, was near 20° C.

Temperature (° C.)	53	72	95	106	117	130	144	160	175
E.m.f. (μV.)	·311	·263	·233	·047	·033	·005	·005	·003	·000

The sudden drop in e.m.f. between 95° and 106° was reversible; in fact in one test the jump of e.m.f. as the temperature dropped was greater than that shown in the above table, which was obtained with progressively increasing temperature.

It will at once be noticed that these results agree, qualitatively, with the positive results obtained before as regards variation with temperature. Further, Benedicks[5] reported his e.m.f. to be of the order of only 0.035μV. for a temperature-difference of 97·5° C. across the constriction. This temperature-difference corresponds roughly with our maximum temperature 117° in the above table, and the e.m.f.

there recorded is almost identical with that of Benedicks. This agreement must be partly fortuitous because the constriction must have caused quite a different temperature-distribution in Benedicks's case.

A rough temperature-analysis was used in an attempt to find homogeneous constants for correlating the three larger e.m.f's. of the above table. No agreement could be found.

This failure is surprising in that mercury is more certainly homogeneous than the other metals in which homogeneous coefficients were found. The most obvious explanation would be that, although the effect is truly homogeneous, the so-called homogeneous coefficients undergo such a rapid decrease with increasing temperature that the methods of analysis here used fail.

However, let us first approach the question in a slightly different manner. Results recently reported for nickel[9] led us to the suggestion that the homogeneous coefficients were really due to nonisotropic properties of the metal; i.e. to regularity in the arrangement of the microcrystals of the metal. It was pointed out that this view does not contradict the homogeneity theory, but merely supplements that theory.

From this point of view, we are led to enquire what factor in the case of mercury can provide nonisotropic regularity of structure in such a homogeneous substance. Evidently the surface layer of mercury molecules is one possible factor. Langmuir's[10] work on monomolecular films of organic substances in contact with glass suggests at least the possibility of regular molecular arrangements in the surfaces even of liquids like mercury. Direct proof of the existence of highly oriented quasicrystalline structure in the surface of liquid paraffin has been obtained by X-ray diffraction methods[11]. We can find no references to investigations on these lines concerning mercury, but it seems plausible to assume that liquid crystals would exist in the surface layer. Such a hypothesis would successfully account for the reversibility of the e.m.f. with respect to temperature-variation.

The connexion between surface quasicrystals and surface tension should be intimate. The work of Burdon[12] on the surface tension of mercury shows a steady decrease of 0·23 dyne per degree up to 230° C.; there is no sudden change near 100° C. corresponding with the sudden change in thermo-e.m.f. observed in the present work. It therefore becomes doubtful if the larger e.m.fs. observed at temperatures below 100° C. can be explained by this surface-crystal theory. It is also doubtful if surface contamination could explain the low-temperature results, because such a hypothesis would hardly be consistent with the good reversibility of the sudden change near 100°.

In fact it seems necessary to postulate the existence within the body of the liquid of quasicrystals whose existence is possible only at temperatures below about 100° C. We hesitate to make this hypothesis because we can find no direct evidence for it in the literature, although the general idea is familiar[13].

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THE THERMOMAGNETIC PROPERTIES OF NICKEL, PART 2

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ABSTRACT. The homogeneous thermoelectric e.m.f. in nickel is examined for various tensions up to 8 kg. in a pure wire of diameter 1 mm. Analysis gives the new constants (Benedick coefficients) as functions of magnetic field and tension. An antisymmetric part of the e.m.f. with respect to the magnetization has been discovered. Evidence suggesting that the effect is controlled by the regularity (anisotropy) of arrangement of the micro-crystals within the wire is given.

§ 1. APPARATUS

The heating-system was the identical set used in the work of Pi and Band on nickel[1]. The temperature mapping followed the same procedure as that discussed in part 1 of this work[2], and in the work of Ch'en and Band on silver[3]. The e.m.f. was modified to yield greater precision and this change constitutes the chief departure in technique from methods already described in previous communications.

In the first place the e.m.f. found was considerably smaller than that previously obtained for nickel[1], and the sensitivity of the modified potentiometer used in that work was not sufficient. To use the galvanometer method employed in earlier work was felt to be unsatisfactory because it was hoped to make use of the present work in a more precise analysis of the results reported in part 1. The latter were obtained by a potentiometer method in which no current is drawn from the specimen under test and a similar arrangement should therefore be adopted in the present work. The following scheme was adopted after several preliminary experiments with alternative systems.

Figure 1 shows the circuit. A controllable working current is maintained in a resistance box B by means of a 2-volt Edison cell and an external rheostat. In parallel with a variable tap in the resistance B is connected a standard 10,000-ohm resistance box S.* The e.m.f. from the specimen is connected in series with a Paschen galvanometer across the 10-ohm section in S, this part of the circuit being provided with a mercury contact switch. All the connexions, the key, and the standard resistance were shielded electrically. The potential-drop across the 10,000 ohms was measured with a K-type potentiometer K with the usual accessories.

The procedure thus consists simply of choosing appropriate plugs in the resistance box B and a finer adjustment of the rheostat R until the Paschen galvano-

* Manufactured by Hartmann and Braun, A.G. Correct to 20° C.

meter indicates zero current through the test wire. The potentiometer K then gives exactly 1000 times the actual e.m.f. required. Since this potentiometer is capable of measuring voltages as small as $0{\cdot}5\mu$V. it is theoretically possible to get a quite fantastic order of sensitivity in this way, provided the Paschen galvanometer is adjusted to have a long period. It is found, however, in practice that fluctuations in the controlled working current make it impossible to maintain a balance of such precision long enough to measure it. It is therefore necessary to be satisfied with as low a sensitivity as permissible, in order to avoid such incidental variations. The galvanometer was adjusted with a period of about 2 seconds, and the potentiometer K was used in its less sensitive arrangement; final e.m.f. readings were recorded only to $0{\cdot}01\mu$V., corresponding to a precision of 10μV. in the potential-difference directly measured by the potentiometer. Balance could be kept easily enough for this purpose.

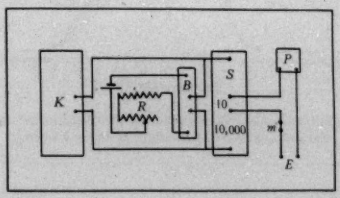

Figure 1. System for measuring e.m.f. K, K-type potentiometer (accessories not shown); R, variable rheostat; B, resistance box, variable tapping; S, standard resistance box, 10,000 Ω.; P, Paschen galvanometer; m, mercury contact key; E, e.m.f. under test.

The open-circuit reading of the Paschen galvanometer was found to be independent of stray fields from outside. Reversal of neither the magnetizing field nor the heating current caused any detectable change. The mercury switch was provided with a sufficiently long handle for manual operation and treated carefully. It caused slight changes, but only during the first few minutes after initial adjustments. Both poles of the switch were kept at the same temperature by keeping the switch closed most of the time throughout the course of the experiments. It was opened only for momentary tests of the open-circuit zero at each null adjustment.

§ 2. RESULTS

Four temperature-distributions were used, figure 2. They were adjusted to correspond in maximum temperature approximately with the distributions studied in part 1. The integrated values A, equal to $\int (dT/dx).dT$, and B, equal to $\int (dT/dx)^2.dT$, for these distributions are given in the following table:

	Temperature map			
	1	2	3	4
$A \times 10^{-3}$	6·7	10·7	11·9	19·3
$B \times 10^{-5}$	5·6	11·5	13·4	27·1

For each temperature the thermomechanical e.m.f. was first found, the combined results being shown in figure 3. There was a slight hysteresis, the return curves lacking the hump in the region between zero and 2-kg. tension, but the final e.m.f. was in each case nearly the same as the initial value. The hysteresis depends upon time, and is evidently connected with elastic recovery after stretching.

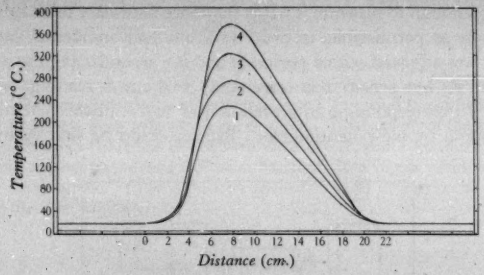

Figure 2. The four temperature maps. (The extent of the centimetre scale coincides with that of the uniform part of the field of the solenoid.)

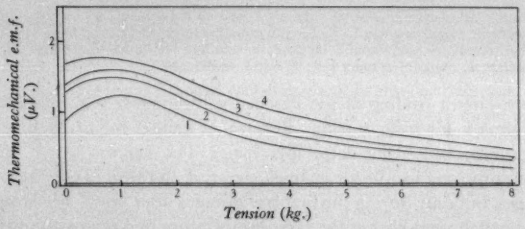

Figure 3. Thermomechanical e.m.f. The numbers refer to the temperature maps of figure 2.

These results were analysed according to the formula

$$E = aA + bB,$$

the method described previously[3]. It gave the curves for a and b as functions of tension shown in figure 4.

The study of thermomagnetic hysteresis at zero tension was next attempted by means of the hysteresis switching arrangement described in part 1. The resulting curve was so complex that it was decided to concentrate attention on the initial rise of e.m.f. with slowly increasing fields before proceeding with hysteresis studies.

This was carried out for both increasing positive and increasing negative fields, where positive field H was directed along AB in figure 2 with respect to the temperature-distribution. Each set of readings was followed by thorough demagnetiza-

tion and the initial reading was checked. The results are shown in figure 5. Contrary to expectation the e.m.f. was found to be greatly different for the reversed H, and a special study was therefore made in the region of small fields. Figure 6 shows these results. For values of the magnetizing current* between 0 and $\mp 0{\cdot}2$ A. the e.m.f. is exactly antisymmetrical with respect to the field; outside of this range the curves are entirely different.

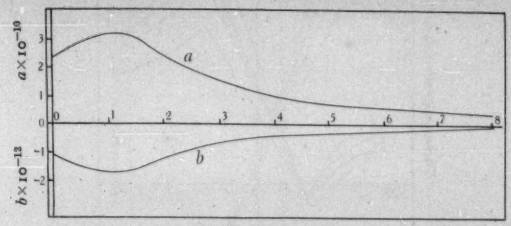

Figure 4. Analysis of the thermomechanical e.m.f.

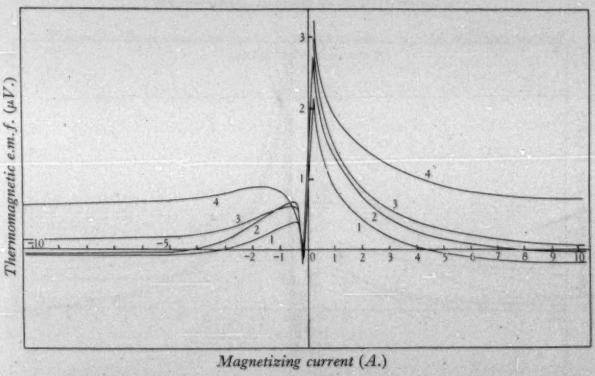

Figure 5. Thermomagnetic e.m.f. Four curves for the four temperature-distributions shown in figure 2. (Zero tension.)

Similar results were obtained for a series of different tensions* up to 8 kg. The values of e.m.f. obtained are summarized in figures 7 to 12. The initial antisymmetry for small fields becomes progressively less with increasing tension.

Analysis of all these data was carried out as before. The resulting values of a and

* A tension of 1 kg. is equivalent to 127 kg./cm^2 and a magnetizing current of 1 A. gives a magnetic field of 303 gauss.

b lie on smooth curves—see figures 13 and 14. On computation from these values the e.m.fs. are in agreement with observed values to within 0·05μV.

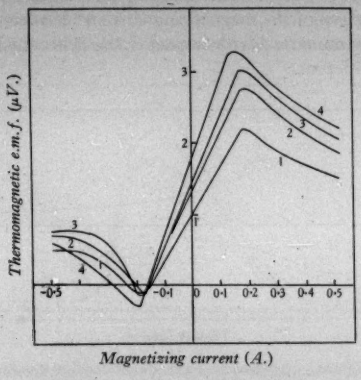

Figure 6. Thermomagnetic e.m.f. Data for a magnetizing field less than 0·5 A.; an enlarged view of the centre part of figure 5. (Zero tension.)

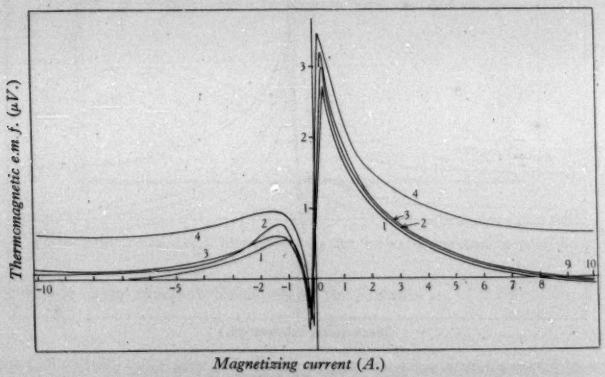

Figure 7. Thermomagnetic e.m.f. with tension 2 kg.

The curves for *a* can be resolved into symmetrical and antisymmetrical parts by the formulae:

$$a_s = \tfrac{1}{2}(a^+ + a^-) \text{ symmetrical,}$$

$$a_a = \tfrac{1}{2}(a^+ - a^-) \text{ antisymmetrical,}$$

where a^+ and a^- mean corresponding values of *a* for equal positive and negative values of *H* respectively. The curves for *b* can be similarly resolved. A plot of a_s,

shown in figure 15, reveals some similarity between the behaviour of these symmetrical parts and that of the Thomson potential-gradient inferred from figure 7

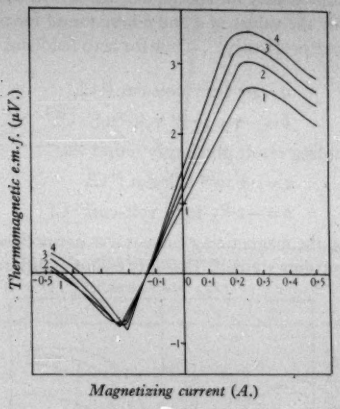

Figure 8. Thermomagnetic e.m.f. with tension 2 kg. An enlarged view of centre part of figure 7.

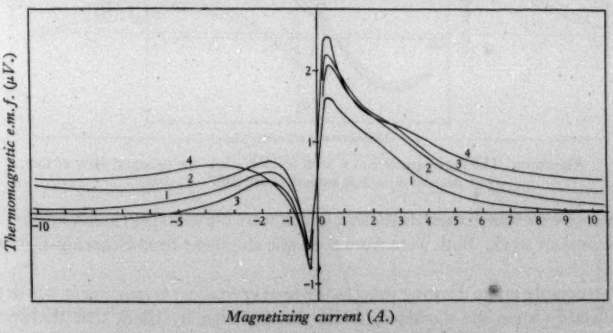

Figure 9. Thermomagnetic e.m.f. with tension 4 kg.

of part 1. The antisymmetrical parts shown in figure 16 are quite peculiar, showing, however, a definite critical magnetic field (at a current of 0·2 A.) which is identical with the field at which the sharp minimum in the hysteresis loops was found in part 1.

§ 3. DISCUSSION

Two points call immediately for special discussion. In the first place the values of the e.m.f. and finally the values of a and b here found for nickel are entirely different from those found previously[1]. Thus for zero field and a tension of 2 kg. the present work gives

$$a = 2{\cdot}5\ 10^{-10}\ \text{volt-cm./}^\circ\text{C}^2,$$

$$b = -1{\cdot}4\ 10^{-12}\ \text{volt-cm}^2\text{/}^\circ\text{C}^3,$$

whereas the corresponding result previously found was

$$a = 1{\cdot}8\ 10^{-9}\ \text{volt-cm./}^\circ\text{C}^2,$$

$$b = -1{\cdot}85\ 10^{-11}\ \text{volt-cm}^2\text{/}^\circ\text{C}^3$$

The effect of reversing the magnetizing current was not noticed previously, nor was the region for small currents studied. The only essential difference between the two

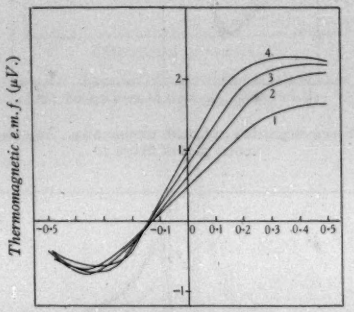

Figure 10. Thermomagnetic e.m.f. with tension 4 kg. An enlarged view of the centre part of figure 9.

samples of wire was in their diameters, which were 0·5 mm. previously and 1·0 mm. in the present work. Both were from the same shipment from Schering-Kahlbaum A.G.

Presumably in the drawing process the final crystalline arrangement will depend considerably upon the diameter. It has been shown by Clark that the drawing process introduces anisotropy in the crystalline arrangement within the wire. These two observations would suggest that perhaps the size and mutual arrangement of the crystals of the metal control the homogeneous coefficients. It should be pointed out, however, that this does not mean that the e.m.f. is not a truly homogeneous effect; the wire must be homogeneous in structure, at least statistically, even though not isotropic. If it were not homogeneous, the analysis used in this work would not succeed: a point which should be clear in the light of results discussed concerning aluminium[5]. However it must be admitted that the constants a and b can no

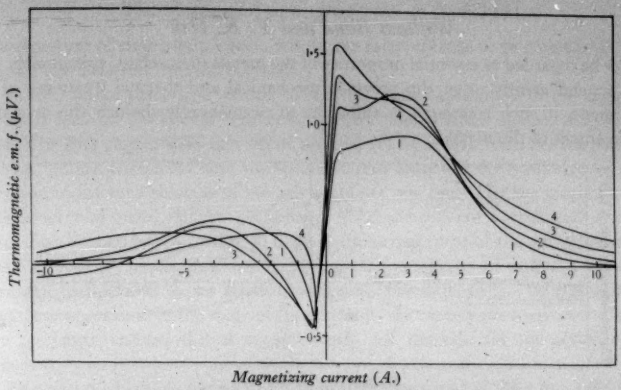

Figure 11. Thermomagnetic e.m.f. with tension 6 kg.

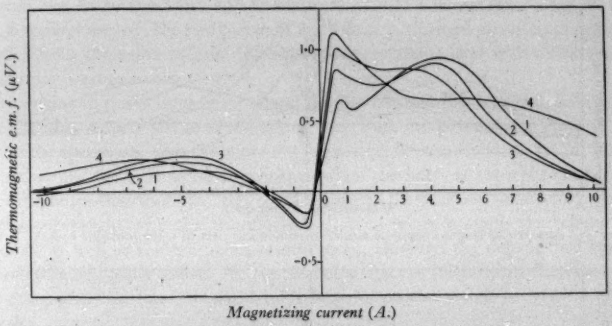

Figure 12. Thermomagnetic e.m.f. with tension 8 kg.

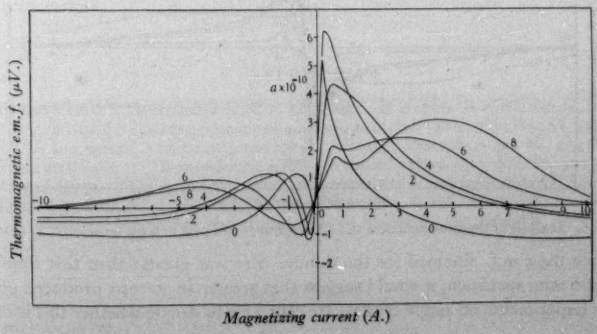

Figure 13. Analysis of thermomagnetic values of a against H for tensions 0, 2, 4, 6 and 8 kg.

longer be regarded as essential properties of the metals themselves; presumably they will depend greatly upon the previous mechanical and thermal treatment of the specimens, if such treatment is sufficient to permanently disturb the crystalline arrangement of the metal.

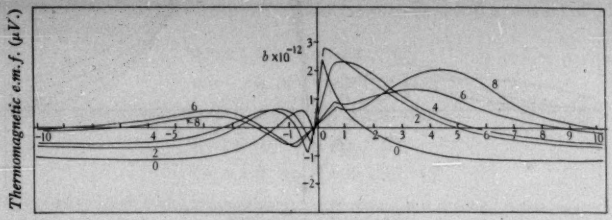

Figure 14. Analysis of thermomagnetic e.m.f. Values of b against H for tensions 0, 2, 4, 6, 8 kg.

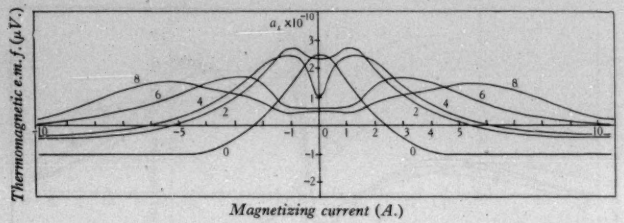

Figure 15. Analysis of thermomagnetic e.m.f. Symmetrical part of a for tensions 0, 2, 4, 6, 8 kg.

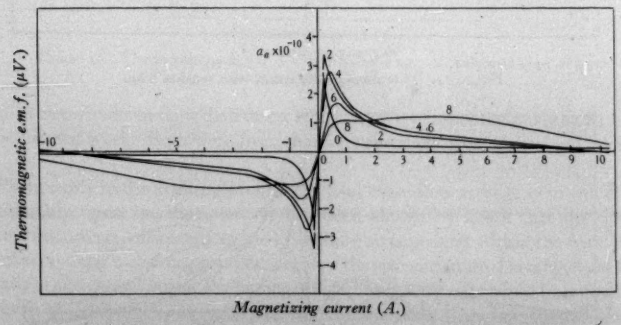

Figure 16. Analysis of thermomagnetic e.m.f. Antisymmetrical part of a for tensions 0, 2, 4, 6, 8 kg.

Since the e.m.f. obtained for the thinner wire was greater than that found for the $-1{\cdot}0$ mm. specimen, it would suggest that greater anisotropy produced greater e.m.f. Experiments on single crystals are called for to decide whether this is due to

an integration of elementary effects within the microcrystals or to contact effects at the surfaces between the microcrystals.

In the second place it is natural to seek for some explanation of the quite unexpected form of the curves representing e.m.f. and a and b against magnetizing field. The first suggestions that occur are that (i) some leak from the magnetizing current became connected with the specimen and disturbed the results, or (ii) some variation of the zero position of the galvanometer was caused by the magnetic field. The latter was ruled out by preliminary (and subsequent corroborative) direct tests. The former seems unable to explain the actual form of the antisymmetry of e.m.f. against H; moreover there is no apparent possibility of mutual contact between the two circuits, as was verified by means of telephone tests. The leak should be directly proportional to the magnetizing current, not merely for small currents, but also for larger values; this is conspicuously not the case for the actual e.m.fs. observed.

Further, the genuine nature of the antisymmetrical part of the e.m.f. (and of the constants a, b) is supported by the coincidence between values of magnetizing current, 0·2 A., in this work and in the work of part 1 where sharp changes in the e.m.f. were observed; the two pieces of work were performed on different specimens of wire from the same roll, in different heating-systems, and with different e.m.f. measuring arrangements.

Speaking in perfectly general terms, we may say that the asymmetrical temperature-distribution, by virtue of the asymmetry, does define a definite sense of direction in the specimen. It is therefore not impossible for the sense or sign of the magnetization also to have some significance when the latter is superposed upon such a temperature-distribution. Up to the present there is no satisfactory physical theory to explain why the thermoelectric force depends upon the temperature-gradient as well as the temperature-difference, although the dependence has been expressed analytically above. We suppose now that the phenomena described in the present paper will have a considerable bearing on the search for such a physical theory.

The correlation of the present results with those of part 1 is reserved for another communication.

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(6) Quoted by Prof. W. L. Bragg, *The Crystalline State*, **1**, 196. No results for nickel are given, but the general phenomena must be fundamentally the same.

537·523·4:534·2

DUST FIGURES FORMED BY AN ELECTRIC SPARK

By A. E. BATE, M.Sc., Ph.D., F.Inst.P.

Received June 28, 1935. *Read, with demonstration, November* 15, 1935

ABSTRACT. The dust figures produced by the sound waves generated by electric sparks passing between a pair of spark gaps in series show interference. Measurements of the patterns made when the distance between the gaps ranged from 15 cm. to 3 cm. show that the wave-length of the sound is constant. When a single spark gap was placed between walls, the sparks produced modified patterns. These are explained by the method of images. The patterns may be regarded as sound maps, and should prove useful in illustrating acoustical phenomena such as the directive properties of cones for high-frequency sound.

§ 1. INTRODUCTION

When an electric spark is passed near a dusty surface the dust is ranged into concentric rings of striae round the spark, the distance between successive rings diminishing as the radii increase. This phenomenon has been the subject of many investigations, among the earliest being those of Mach and Rosicky[1], and among the more recent those of Richmond[2], Robinson[3], Marsh and Nottage[4], Campbell and Dye[5], and Barton and Kilby[6]. The conclusions to be drawn from these papers are as follows: (*a*) The striae are due to hydrodynamic forces set up by sound waves. (*b*) The frequency of the sound waves is not necessarily the same as that of the spark. (*c*) The spacing of the striae varies with the intensity of the disturbance producing them.

The writer repeated the investigation and extended it to the formation of figures by two and three sparks in series, and those formed when a single spark was enclosed between walls.

§ 2. APPARATUS

The apparatus consisted of a coil and condensers for the production of the sparks, spark gaps which could be arranged to give two or three sparks in series, levelling-screws, and plane glass plates, some of which were formed with holes about 1 cm. in diameter to allow a complete pattern to be produced round a vertical spark.

§ 3. PROCEDURE

Single sparks. One of the plates was cleaned, levelled and lightly dusted with dried lycopodium spores which had been sifted to produce uniformity of size. After the lower point of the gap had been set level with the surface of the glass, several sparks were passed through the hole in the plate. As has already been stated, the

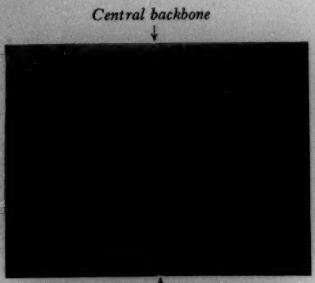

Figure 1. Pattern formed by twin sparks in series, 15 cm. apart.

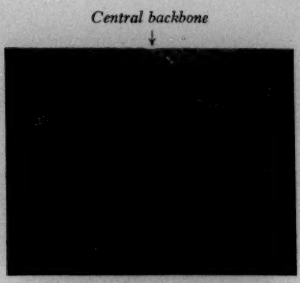

Figure 2. Pattern formed by twin sparks in series, 4·5 cm. apart.

Figure 5(*a*). Pattern formed in a rectangular enclosure by a spark from a single source.

Figure 6. Pattern formed in a horn section (p. 180), spark at narrow end.

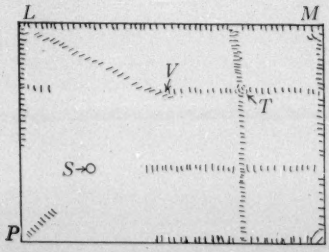

Figure 5(*b*). Key to figure 5(*a*) showing main features only.

To face page 179

resulting pattern was made up of concentric rings of powder with the spark as centre. Prolonged sparking only served to accentuate the patterns and to remove the powder from the vicinity of the spark.

Double sparks. Two sparks in series gave patterns which show interference effects, figures 1 and 2. Each of these patterns was produced by sparking under identical conditions except that the sparks were at different distances apart, the positions of the sparks being indicated by the absence of powder. Interference implies the propagation of waves by both sparks.

The striae in the patterns follow a general form. Midway between the sparks and at right-angles to the line joining them is a backbone in which two sets of striae occur. In interpreting these it must be remembered that the resultant effect of the

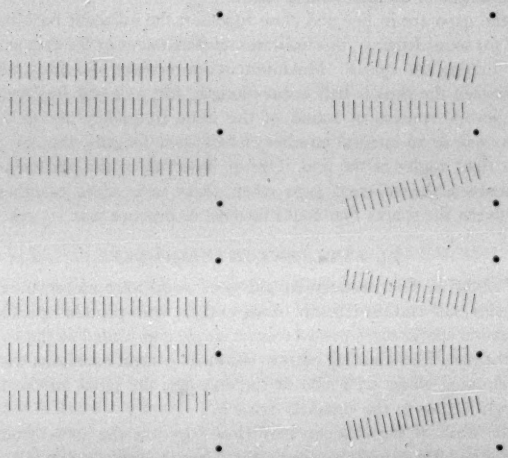

Figure 3. Patterns developed by three sparks in series. Spark gaps are denoted by dots.

sparks is at right angles to the direction of the striae. The striae nearer the sparks indicate that standing waves are set up between the latter. Farther out along the backbone the striae are parallel to the line joining the sparks, and thus indicate reinforcement of the waves, which must be progressive. Adjoining the backbone are areas in which the powder is undisturbed, and these are succeeded by areas showing reinforcement. The areas in which the powder is not disturbed are zones* of interference in which the distances of a mean point from each spark differ by half a wave-length. Measurements of patterns in which the sparks were separated by distances varying from 1·5, 3·0, 4·5, ..., up to 15 cm. gave $\lambda = 1{\cdot}7$ cm.

* When the gaps are close together, the contours of the dust-clear areas show the directions of interference and reinforcement.

These results were obtained on the assumption that the velocity of the sound was constant. Actually the velocity is greater near the spark but falls rapidly to the normal. Foley[7] found that the velocity of a pulse from an intense spark fell rapidly from 660 m./sec. at 3 mm. from the spark to almost normal at 18 mm., and that the initial velocity varied with the intensity of the spark. The sparks used in the present experiments were less intense than those of Foley, and it is probable that no appreciable error arises in consequence of the assumption that was made.

Three gaps. Three equal gaps in series were next used; their positions and those of the resulting striae are shown diagrammatically in figure 3 for four different arrangements.

All patterns showed the backbone striae midway between each pair of sparks and at right angles to the line joining them.

When the gaps are in line and close together, the adjacent backbones overlap and extend for some distance; this indicates reinforcement in the area at right angles to the line joining the sparks. Maximum reinforcement should occur when the distance between the gaps is half a wave-length, for, as Lord Rayleigh[8] pointed out, when several sources of sound of the same frequency are in line and are separated by one or an integral number of half-wave-lengths, they project a beam of sound at right angles to the line. Owing, however, to the occurrence of direct sparking between the adjacent gaps when these were close together, the least distance between the sparks that could be used in practice was 1·5 cm.

§ 4. PATTERNS IN CHANNELS

Parallel channels. Two rectangular pieces of wood were placed parallel to each other on a glass plate and the channel between them was sprinkled with lycopodium powder. Several sparks were passed from a single gap placed at the centre of one end of the channel. The resulting pattern showed a central backbone with narrower backbones running along each side of the channel, the striae in the three being ranged at right angles to the channel, figure 6.

When the walls of the channel were close together the striae from the three backbones met to form a single backbone, but when the walls were a few centimetres apart the powder which lay between the backbones was ranged into striae along the channel, and indicated the presence of standing waves. The distance between the walls and the adjacent set of longitudinal striae, being $\lambda/4$, may be used to determine the wave-length.

An interesting pattern was obtained when the spark gap was a centimetre or so from the axis of the channel, for four sets of striae appeared, figure 4(*a*), one along each wall, the third along a line through the spark gap, and the fourth symmetrically placed with respect to the third. These patterns can be explained by applying the method of images. Let AB and CD, figure 4(*b*), represent the walls and S the spark gap. Denote primary and secondary images by S_1, S_1', S_2, S_2', ..., the secondary of S_1 being S_2 and so on. Suppose S and S_1 to be isolated sparks; then the resulting backbone striae will lie midway between them, i.e. along AB. Similarly S and S_1' will give rise to the striae along CD, S_2 and S_2' to SX, S_1 and S_1' to TY;

and it is obvious that the other pairs of images reinforce either of the existing four backbones. When the spark is central, SX and TY coincide.

Inclined channels. If the sides of the channel are not parallel, the four backbones appear, but lie on lines which radiate from the point at which the walls would intersect if produced; two lie along the walls, and the other two are symmetrical, one passing through the spark gap.

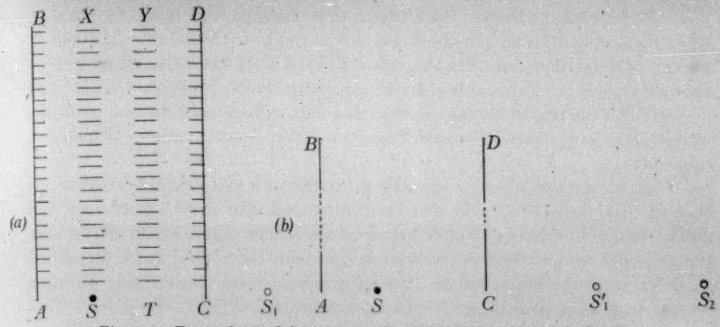

Figure 4. Eccentric spark between parallel walls; (*a*) main features of striae, (*b*) mirror images of spark *S*.

§ 5. PATTERNS IN RECTANGULAR ENCLOSURES

Patterns formed by a series of sparks from a spark gap in a rectangular enclosure show that the parallel-channel effects due to the opposite pairs of sides are superposed, and that these are modified by the inclined-channel effects arising from the adjacent pairs of sides, figure 5(*a*). Thus the focus at T, figure 5(*b*), is due to the intersection of the backbone striae, and the inclined backbone LV is due to the inclined sides LM, LP. Finally, the standing waves due to reflection at the walls account for the striae parallel to the walls; these striae coupled with the inclined backbones undoubtedly explain the dimpled appearance of the pattern.

When the walls were covered by a glass ceiling the general form of the patterns remained the same, but the spacing of the striae was modified.

§ 6. SIGNIFICANCE OF THE PATTERNS

These patterns may be regarded as maps of sound, and should be useful in predicting the acoustical properties of an enclosure. If the floor of a three-dimensional scale model of an auditorium be sprinkled with powder and sparks be passed at the point corresponding to the position to be occupied by the speaker or other source of sound, the resulting pattern on the floor is sensibly a map of the sound pattern developed at the level of the ears of an audience. Different wave-lengths may be tested by altering the wave-length of the spark-pulse or by maintaining a constant spark and altering the scale of the model. The effect of draping may be simulated by attaching felt to the model.

§ 7. HORN SECTION

The method was used to trace the path of sound along the section of a horn with curved sides and a curved axis. Two small blocks were shaped to resemble the sections of the sides of such a horn and were placed on a glass plate at suitable distances apart. After the plate had been sprinkled with powder, sparks were passed at the narrow end of the channel. The experiment was repeated with various distances between the blocks. The patterns thus obtained were found to differ, for when the channel was narrow the striae curved round the bend at right angles to the axis of the section, but when the width of the channel was increased the pattern showed a distinct reflection at the concave bend, which probably indicates the presence of a filtering or resonance effect in a horn of this width for the particular wave-length used. Davis[9] noticed this in his experiments on a horn section in a ripple tank.

When the axis of a horn is straight, the pattern formed resembles that of the channel with inclined sides in that the central and wall striae are present, but differs from it in that the longitudinal striae are absent, figure 6. It will be seen from the photographs that the wall striae join with the central striae for only a short length of the horn, but that the latter persist for a considerable distance. Thus a large horn projecting a short wave-length has directive properties. This was pointed out by Rayleigh[10] many years ago; he showed that a cone will concentrate a hiss, that is a high-frequency sound, in the direction of its axis for a considerable distance if the diameter of its wide end be large in comparison with half the wave-length of the sound.

Since inclined sides project sound but parallel sides do not, a straight horn of rectangular section with one pair of opposite sides parallel and the other pair inclined will project sound along the axis in a fan-shaped path in a plane at right angles to the triangular sides of the horn. This result also is in accordance with Rayleigh's observations[11].

§ 8. ACKNOWLEDGMENTS

The writer wishes to record his appreciation for suggestions and helpful criticism by Dr Marsh, of Battersea Polytechnic, in whose laboratory the major portion of the experimental work was performed.

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DISCUSSION

Lord RAYLEIGH said that it was difficult to understand how a sound like the snap of a spark could have a definite wave-length.

Dr W. A. LEYSHON asked whether the frequency of the waves might be determined by a mechanical vibration of some solid part of the apparatus.

Dr BRUCE CHALMERS. The author has not mentioned what seems to me the most interesting aspect of his work, that is, the cause of the phenomena which he ascribes to interference. The dust figures cannot be due to the accumulation of dust at either the nodes or the antinodes of stationary-wave systems, since their spacing depends upon the intensity of the disturbance, and so cannot be equal to the half wave-length at every part of the figure. Hence the interference phenomena are not due to the interference of trains of waves. The formation of the striae seems rather to be analogous to the formation of the transverse ridges in a resonating Kundt's tube, and is clearly due to the interaction between the moving air and the stationary surface, perhaps by the formation of vortex filaments between which the dust collects. The fact that interference effects are obtained when two such systems are superposed might throw some new light on the dynamics of the formation of the figures.

AUTHOR'S reply. In reply to Lord Rayleigh: This point was raised in the discussion following Marsh and Nottage's paper[4] and it was there suggested that the sound consists of a short train of waves, perhaps twenty in number. The interference patterns in the present experiments indicate that part of the train is of sufficient amplitude to produce striae, or ripples.

In reply to Dr Leyshon: It is possible that mechanical vibrations are set up in the electrodes, particularly as all the pairs of rods forming the gaps were of the same dimensions. The suggestion will be tested by using rods of different lengths.

In reply to Dr Chalmers: The explanation given in the paper appears to have been misunderstood. The distance between successive ripples is not equal to half the wave-length, for the ripples are produced by sparks from a single gap, from which no stationary-wave system would be expected to arise. They are clearly due to the same effect as those in a Kundt's tube. The question of interference arises when two sparks are passed simultaneously, for the backbone which persists midway between the sparks has a narrow zone on each side in which the dust is undisturbed. The backbones indicate reinforcement and the zones indicate interference, the difference between the distances from the sparks to a mid-point in either of the zones being half a wave-length.

I wish to thank Mr Lucas and Dr Bartlett for drawing my attention to a paper by Dr E. H. Cook* which deals with the formation of the concentric rings by sparks from a single gap.

* *Proc. phys. Soc.* **9**, 371 (1888).

535.421

SOME PRELIMINARY NOTES ON DIFFRACTION GRATINGS

By F. F. P. BISACRE, O.B.E., M.A., B.Sc.

Received October 4, 1935

ABSTRACT. In § 1 a simple test, using polarized light, for the best setting of a diffraction grating is described. When used under the best conditions for brightness, a grating should show little or no polarizing effect. The reason for this depends upon the fact that the Huygens-Kirchhoff integrals for the electric and magnetic vectors have different cosine factors which have the same value only in the case of ordinary reflection. In § 2 an extension of the Huygens-Kirchhoff integrals bringing in a second approximation is given. This second approximation becomes important if either the radius of curvature is comparable to the wave-length of light or the angle of incidence is very nearly 90°, as it may be in soft X-ray experiments. In § 3 a new curve for the effect of slit-width upon the resolving-power of a spectroscope is given and compared with Schuster's curve also. Schuster's curve is based on the assumption that the slit is filled with incoherent light; the author's, with coherent light. These two curves are probably upper and lower limits. In § 4 a new method of ruling concave gratings, namely radial ruling, is suggested. In this method the diamond is given a uniform chordal displacement, from line to line, as in the present method of ruling, but during its displacement from line to line it is constrained to rotate about an axis parallel to the ruled lines and passing through the centre of curvature of the face of the grating. For the metal concave grating of more than 20,000 lines per inch this method of ruling would do what figuring does for an astronomical mirror, though not to so high an order of accuracy.

§ 1. THE POLARIZING PROPERTY OF DIFFRACTION GRATINGS

In the study of the radiation reflected from gratings it is usual to use some form of Huygens-Kirchhoff surface or line-integral, for instance, in the two-dimensional problem

$$\int \frac{e^{-i\alpha(R+\rho)}}{\sqrt{(R\rho)}} \cos \widehat{Rn}\,.\,ds \approx \frac{\cos \widehat{Rn}_0}{\sqrt{(R_0\rho_0)}} \int e^{-i\alpha(R+\rho)}\,ds,$$

α, λ, R, ρ, ds, $\widehat{Rn}$

where α is $2\pi/\lambda$, R the distance from the line source and ρ the distance from the field point to the element ds, and $\widehat{Rn}$ is the angle between the line R and the normal n at the element ds. The integral is taken over the live parts of the cross section of the grating. This, or an equivalent, integral is used in the literature for calculating both the electric and magnetic vectors. It seems not to have been noticed that a distinction should be made; for the electric vector the cosine factor is $\cos \widehat{Rn}$, while for the magnetic vector it is $\cos \widehat{\rho n}$.

These quantities are the same only for ordinary reflection ($\widehat{Rn}_0 = \widehat{\rho n}_0$). The explanation of the polarizing properties of a grating lies here. Rowland has stated that metal gratings of 20,000 or more lines per inch consist wholly of grooves with no

flats between them. Such gratings would show little or no polarizing effect if they operated under the best conditions for brightness, so that the sides of the active groove reflected as ordinary mirrors, and $\widehat{Rn}_0 = \widehat{\rho n}_0$. This provides a simple test of the best setting of a grating, for it is very easy to examine the light for polarization.

§ 2. AN EXTENSION OF THE HUYGENS-KIRCHHOFF INTEGRAL

These integrals are first approximations, more or less close, to the exact values. Certain experimental evidence exists suggesting that these integrals may be seriously wrong if very small glancing angles of incidence or reflection are in question, such, for instance, as may arise if a grating is used at very sharp grazing angles. These are the conditions which hold when glass gratings are used for determining the wave-lengths of soft X rays. The results differ by a small but unwelcome amount from measurements made with crystals.

A second approximation to the exact solution in terms of integrals of the above type has been calculated by the writer. It turns out that it is obtained by merely introducing a factor into the integrand.

This factor is

$$\left(1 - i.\frac{\sec^3 \widehat{Rn}}{2\alpha r}\right) \quad \text{for the electric vector,}$$

and

$$\left(1 + i.\frac{\sec^3 \widehat{Rn}}{2\alpha r}\right) \quad \text{for the magnetic vector,}$$

with the change in the cosine factor to $\cos \widehat{\rho n}$ instead of $\cos \widehat{Rn}$ already mentioned. The symbol r represents the radius of curvature of the contour at the element ds. This factor shows at once the order of the error that may be expected. It may be important if either the radius of curvature is comparable to the wave-length *or* the angle of incidence is very nearly 90°, as it is in the soft X-ray experiments mentioned. In these circumstances, the situation is only saved if λ/r is a sufficiently small number, and it must be *very* small indeed as $\widehat{Rn}$ approaches 90°. If, for instance, a lightly ruled glass concave grating is used, reflecting only from the untouched polished glass between the rulings, r is finite, and the error will become important if $\widehat{Rn}$ is sufficiently near to 90°. If plane gratings are used, the limit is likely to be much closer to 90° since the radius of curvature of the facets is probably much greater. Distortion due to ruling may prevent the facets from being quite flat, so that r is not infinite. The correction may thus be important in experiments on soft X rays with ruled plane or concave gratings, especially if a high accuracy is claimed for the results.

§ 3. THE EFFECT OF SLIT-WIDTH UPON RESOLUTION

It has long been recognized that the theoretical resolution of a grating for monochromatic radiation, namely

$$\lambda/\delta\lambda = rM,$$

where r is the order of the spectrum and M is the number of times, applies only for an infinitely narrow slit.

Actually, for finite slits

$$\lambda/\delta\lambda = rM \times y,$$

y, x where $y = F(x)$ and $x = 2u\sigma/\lambda,$

u, σ, λ $2u$ being the angular aperture of the apparatus, σ the slit-width and λ the wave-length.

Wadsworth published[1] values of y, the "purity factor", in 1897. The papers revealed an alleged optimum slit-width at $x = 0{\cdot}2$, where $y = 1{\cdot}09$. Some years later Schuster[2] published another table of values of y. His table showed no optimum slit-width. The paper led to a good deal of discussion at the time.*

Both Wadsworth's and Schuster's calculations were based on the assumption that the slit is filled with a set of completely incoherent Huygens sources of uniform strength. The differences in their tables were due to the differences in the methods of mathematical approximation, and a recalculation by the writer has confirmed Schuster's figures. But there is an alternative limiting assumption—the slit may be filled with a series of completely coherent Huygens sources of uniform strength. Since the disturbance at any point P in the slit, due to any single external point source of radiation, is a continuous function, as to both amplitude and phase, of the position of the point P in the slit, it follows that the same is true for the resultant disturbance due to any number of external point sources acting simultaneously, whether these sources be atomic radiators or sources of any other type. Consequently the phase-changes across the slit must be free from the haphazard discontinuities contemplated in the idea of complete incoherence. Some degree of coherence there must be; the question is, how much? The answer to this question depends upon the distances of the sources from the slit, the size of the slit, and the wave-length. With narrow slits, comparable in width to the wave-length, complete coherence may be closer to the truth than complete incoherence, while for wide slits the opposite may be true. The question arises—are the values of y appreciably different for the two alternative assumptions? The writer has made the necessary calculations and finds that with complete coherence in the slit the resolution is improved for narrow slits, the underlying reason being that the wave-fragment passing through the slit is fringed appreciably with ripples of phase and amplitude. These ripples sharpen the image of the slit and enable two images closer together to be resolved by the Rayleigh rule. These effects disappear as the slit-width increases.

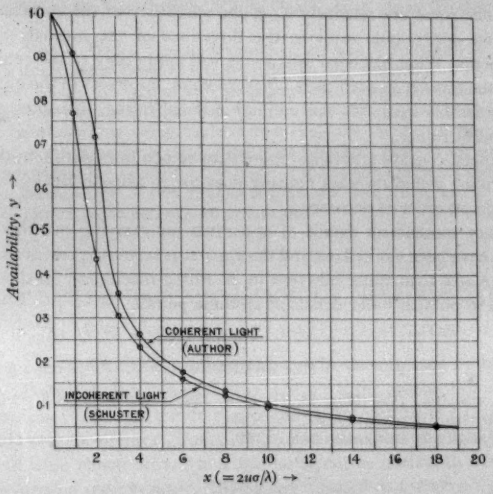
It is just in the case of narrow slits that complete coherence of the light is conceivable for the reasons already given. Probably the truth lies somewhere between these limiting cases—it is a matter for experiment to decide, but suitable experiments have not, apparently, been described. The curves give the results and show that considerable differences in the value of y occur when $1 < 2u\sigma/\lambda < 3$. In the illustration the word "availability" is used instead of "purity", for this factor shows how much of the theoretical resolution rM is available at any particular value of $2u\sigma/\lambda$.

* See, for instance, reference (3).

§4. RADIAL RULING FOR CONCAVE GRATINGS

In the ordinary method of ruling a concave spherical grating, the diamond is given a uniform chordal displacement from line to line as a rigid body. No rotation of the diamond takes place, theoretically at all events.

Suppose, for the moment, that the lines are short enough in comparison with the radius of curvature of the face of the grating, to allow us to consider the surface ruled upon as cylindrical instead of spherical. In these circumstances, the normals to the active sides of the grooves are all parallel, and the width of the active sides of



Effect of slit-width on resolution.

the grooves increases from one side of the grating to the other, for a uniform depth of line. Now for optimum brightness, the normal to each active side of a groove should bisect the angle between the lines joining the centre of the groove-side to the slit and the spectral image. The side of the groove will then operate as an ordinary mirror and the total effect at the image will be the cumulative effect of all the active sides of the grooves.

The directions of the normal should, then, change in crossing the grating. Actually, as the grating is ruled, they do not and there is an error in respect of the best direction of the normals. This error is expressible as a power series in θ, the polar angular coordinate of the side of the groove, and the series begins with a first-order term in θ. The first-order term would be completely eliminated if the diamond, during its displacement from line to line, were constrained to rotate about an axis parallel to the ruled lines and passing through the centre of curvature of the face

of the grating; instead of without rotation, as in the usual method of ruling. The truth of this is immediately obvious in the case of a Littrow mounting. Uniform chordal displacement from line to line would, of course, be preserved.

All that is necessary, mechanically, for ruling in this way is to provide a curved guide-way for the diamond-holder instead of the usual straight guide-way. The curvature of the guide-way is the same as the curvature of the face of the grating.

If the grating is ruled in this way, the active sides of the grooves have their normals correctly directed up to errors of the second order, and the lengths of the active sides of the grooves are much more nearly uniform.

If the lines ruled are relatively long, the sphericity of the surface ruled upon will introduce appreciable error in the directions of the normals to the outer groove elements. What has been said above will apply only to the central parts of the sides of the grooves in such cases. Nevertheless, the errors in the outer elements will be considerably less, with this method of radial ruling, than they are with the usual method of ruling.

For the metal concave gratings of more than 20,000 lines per inch, the proposed method of ruling would do what figuring does for an astronomical mirror, though not to so high an order of accuracy.

Preliminary mechanical details of apparatus for carrying out this method of radial ruling have been worked out and the apparatus seems to present no mechanical difficulties greater than those inherent in all ruling-machines. In due course the writer hopes to publish fuller details of all these points.

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THERMOCHEMICAL PROPERTIES OF NITROUS OXIDE

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ABSTRACT. Part I: With a view to determining the heat of formation of nitrous oxide by means of a direct decomposition into its elements, the conditions of initiation and of pressure under which this action will propagate itself progressively and explosively through the gas has been examined. Part II: The heat of formation of nitrous oxide has been directly measured, use being made of this explosive thermal decomposition. The figure obtained is 19·52 ± 0·1 Cal./mol. at constant pressure. Part III: A simple method is given for comparing the values for two gases of the product pressure × volume, and is applied to the measurement of this product at pressures between 10 and 45 atmospheres in the cases of nitrous oxide and of carbon dioxide.

PART I: THE DECOMPOSITION OF NITROUS OXIDE

By H. R. AMBLER and T. CARLTON-SUTTON

It has long been known that nitrous oxide can be decomposed by heat, and that a burning body will decompose it progressively if the combustion is sufficiently hot. Berthelot[1] effected the decomposition of nitrous oxide by compressing it very suddenly to 1/500 of its original volume. A less drastically applied compression, however, had little effect, although it was sufficient to initiate the explosion of a mixture of hydrogen and oxygen[2]. Maquenne[3] stated that when 0·1 g. of mercury fulminate was detonated in one atmosphere of nitrous oxide, the gas was decomposed with sufficient violence to shatter the vessel in which it was contained. Houseman[4] stated that "when under pressure (e.g. in the saturated state) decomposition may be propagated throughout the entire mass of N_2O with explosive violence; if the compressed gas has a temperature above the critical value (38·8° C.) this method of ignition", i.e. ignition by means of heated iron or platinum wire, "seldom fails to cause explosion"; exact figures and experimental details were lacking however.

Our experience with this gas was not in accord however with the above statements, and a further investigation was undertaken. This has shown that decomposition is not propagated at pressures below 13 atmospheres but can be propagated at pressures above 13 atmospheres.

When small quantities of lead azide were detonated in atmospheres of nitrous oxide at various pressures, it was found that the proportion of nitrous oxide de-

composed increased rapidly with increase of the initial pressure, and that at the higher pressures the explosion was complete and was an intrinsic property of the nitrous oxide itself. For example, while decomposition does not occur at atmospheric pressure, 10 per cent of the nitrous oxide is decomposed at a pressure of 10 atmospheres and more than 99 per cent is decomposed at pressures above 35 atmospheres.

A simpler method of initiation was found in the fusing of an electrically heated platinum wire. The initiation was not due entirely to the energy supplied to the wire and the temperature attained by it, since the fusion of a wire in a low-voltage, low-resistance circuit of low inductance was not sufficient to cause explosion. Explosion was obtained, however, when the production of a spark on the fusing of the wire was ensured by either (i) the introduction of additional inductance and capacity, or (ii) an increase of the voltage above 20. The initial temperature was approximately 20° C. throughout.

As will be seen from table 1, the pressure which determines whether explosion is propagated lies between 12 and 15 atmospheres.

Table 1

Initial pressure of nitrous oxide (atmos.)	Number of determinations	Nitrous oxide decomposed (per cent)	
		Extreme values	Mean values
2			<1
5			
7			
10			
11	3	1·3–7	4
12	3	9–35	23
13	4	0·5–85	41
14	3	66–89	
15	1		88
30	2	91–95	93
37	1		91
42	6	91–93	92
48	1		>93

PART II: MEASUREMENT OF THE HEAT OF FORMATION OF NITROUS OXIDE BY DIRECT DECOMPOSITION

By T. CARLTON-SUTTON, H. R. AMBLER and G. WYN WILLIAMS

§ 1. HISTORICAL

The measurement of the heat of formation of nitrous oxide has become important in recent years on account of its being a datum in the determination of the specific heats of gases at high temperatures. Hitherto the heat of formation has been deduced from measurement of the heat produced when nitrous oxide reacts with

hydrogen or with carbon monoxide. Whichever of these reactions is used, some 80 per cent of the heat measured comes from the oxidation of the combustible gas, the heat of formation of the nitrous oxide contributing the remaining 20 per cent; any error in the thermal measurement will therefore be magnified by about five.

Figures which have been obtained for the heat of formation of nitrous oxide by these combustion methods are given in table 2. The present writers have also used these methods, employing pressures of about 50 atmospheres; the figures which have been obtained and the causes which have made the procedure unsatisfactory at these pressures are discussed in § 4.

Table 2. Determination of heat of formation of nitrous oxide by combustion methods

Observer	Method	Heat of reaction $(\text{Cal./mol.})_{cp}$	Deduced heat of formation of nitrous oxide $(\text{Cal./mol.})_{cp}$
Berthelot[5]	Combustion with CO at constant volume	88·2	−20·6
Thomsen[6]	Combustion with H_2 at constant pressure	86·3	−18·01
Thomsen[6]	Combustion with CO at constant pressure	85·1	−17·47
Awbery and Griffiths[7]	Combustion with CO at constant pressure	87·1	−19·5
Fenning and Cotton[8]	Combustion with CO at constant volume; pressure about 5 atm.	87·4	−19·75
Fenning and Cotton[8]	Combustion with H_2 at constant volume; pressure about 5 atm.	88·0	−19·74

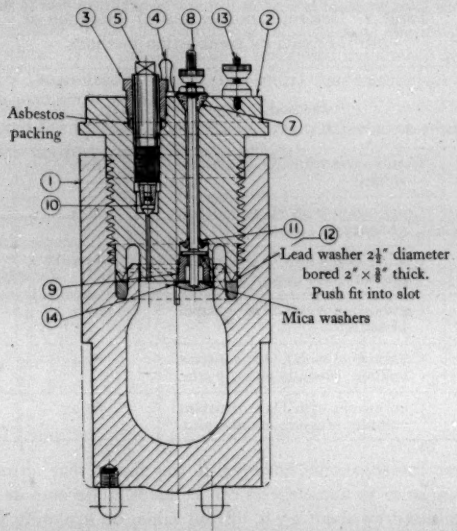
During these investigations, however, it was found that nitrous oxide at a pressure of from 40 to 50 atmospheres can be made to decompose as a mild explosive when initiated by about 0·5 g. of lead azide; on exploring further, it was found that the decomposition can also be produced by fusing a wire in the compressed gas, provided the applied voltage is sufficient to give an arc as the circuit breaks. The latter method has now been applied and will be detailed here.

§ 2. EXPERIMENTAL

Method. Nitrous oxide at a pressure of approximately 42 atmospheres was exploded in a calorimetric closed vessel of stainless steel. The heat produced was measured according to a procedure developed in connexion with the calorimetry of propellants and with which measurements are habitually made to one part in a thousand[9]. Two mercury-in-glass thermometers[10], calibrated to 0·001° C. and certified to 0·002° C.*, were used.

* N.P.L. Ref., Th. 13319.

The closed vessel contained initially nitrous oxide, which was found on analysis to be substantially pure, and finally a mixture which was found to correspond to a decomposition of 90–95 per cent of the original nitrous oxide. The measurement of the heat of formation depended therefore on the precise determination of the quantity and composition of these final products. To determine the mass of nitrous oxide decomposed, three possible methods were available: (i) weighing the nitrous oxide originally taken and determining the amount of nitrous oxide which remained undecomposed; (ii) determining the total free nitrogen produced; and (iii) determining the total free oxygen produced.



Method (i) is limited by the necessarily large mass of the containing vessel, which necessitates the use of a balance capable of taking a load of 10 kg.* It involves also a difficult and somewhat unsatisfactory determination of nitrous oxide in the final gases. As nitrogen is habitually determined by difference, method (ii) also involves this unsatisfactory determination of nitrous oxide in the final gases. Method (iii) is free from these objections, in that the oxygen may be determined directly. The presence of nitrous oxide, however, seriously affects the accuracy of the standard methods of accurate measurement of oxygen-content hitherto employed. This problem has been investigated at some length therefore in this laboratory, and methods have now been evolved for measuring the oxygen-content of the initial and of final gases to within 0·1 per cent.

* The mass of nitrous oxide was approximately 15 gm. See table 6.

The heat of formation has been calculated by each of the three methods. The most accurate figure, that given by method (iii), table 6, has been confirmed, table 7, by methods (i) and (ii) within the accuracy obtainable by these latter methods.

Closed vessel. The closed vessel, illustrated in the diagram, was made of Staybrite steel and had a capacity of 128 cm^3. The main seal 12 was made by means of a steel knife-edge and lead washer. The lead was protected from the action of the hot gases by the presence of two narrow annular passages, 0·015 in. and 0·005 in. wide respectively, through which the hot gases had to pass before reaching the lead; by this means the gases were sufficiently cooled, before coming into contact with the lead, for the lead to be unattacked. Inspection of the seal after each experiment showed that no oxidation of lead had occurred.

Water equivalent of calorimetric apparatus. The closed vessel was one of a number used in the calorimetric examination of propellants. When the water equivalent of these was being measured, the possibility of erroneous effects due to reactions between the gases and the steel surfaces was considered, and a diversity of methods were employed for the determination of the water equivalent under varied conditions. These determinations are summarized in table 3, and the effect of the reactions is seen to be inconsiderable.

Table 3. Determination of water equivalent

Method	Water* equivalent (g.)	Number of determinations	Mean difference from mean
Firing 1 g. benzoic and salicylic acids in 100 atm. of oxygen	3769	10	5
Exploding gaseous mixtures containing 22 atm. CO, 11 atm. N_2 and 67 atm. O_2 and determining the CO_2 produced	3771	4	4
Comparing with standard vessel† by firing charges of cordite in an inert atmosphere	3774	4	6
Accepted figure	3771		

* Adjusted to water equivalent = 3 g.

Nitrous oxide. Nitrous oxide of very high purity can now be obtained commercially; the gas used for these measurements was stated by the makers, Messrs Coxeter, London, to be 99·995 per cent pure. A sample for analysis was taken from the closed vessel before firing, and tested for oxygen by a sensitive colorimetric method described elsewhere[11]. In no case was a figure greater than 0·05 per cent of the nitrous oxide obtained. This procedure served the dual purpose of checking the composition of the nitrous oxide and of showing whether any air had become mixed with it during the process of filling.

Filling of closed vessel. At the beginning of an experiment, the closed vessel, containing 1 cm^3 of water‡ and one atmosphere of air, was weighed. It was then

† The water equivalent of this vessel had been determined both electrically and by the combustion of carbon monoxide[9].

‡ In order to absorb the small quantities of higher oxides of nitrogen in the products.

evacuated and filled two or three times with nitrous oxide to about 10 atmospheres and the gas released. It was finally filled to about 45 atmospheres.

Method of initiation. Decomposition was initiated by fusing at 50 volts a platinum wire 3 cm. long and 0·012 cm. in diameter. The voltage could be lowered, however, if the production of an arc on fusing was assured by a strongly inductive circuit. The wire was attached by small grooves to two rods of Staybrite steel fixed to the head of the closed vessel. To fire the charge, the circuit was completed and the switch was kept in until, as was shown by an ammeter, the wire fused.

In blank experiments in which the nitrous oxide was replaced by nitrogen or oxygen, the heating effect (4 cal.) was insufficient to be clearly measurable even when it had been magnified by replacing the wire by two similar wires connected in parallel. When a system of smaller thermal capacity was used in the same way, however, rises of 0·004° C. and 0·003° C. were observed, the firing-currents being 8 A. and 6 A. respectively. These rises corresponded to 8 cal. and 6 cal., i.e. to approximately one calorie per ampere. Since this quantity is a small proportion of the total heat, a correction at this rate has been considered adequate.

Measurement of total gas. After each calorimetric measurement, the volume of the final gases was measured by connecting the closed vessel with an evacuated bottle and reading the rise in pressure. The bottle was one of a series of measured volume which are used regularly[12] for measuring the volumes produced on burning propellants of various compositions. The volumes of the constituent gases were obtained by analysing samples taken separately from the bottle and from the closed vessel*.

Analysis of final products. Gases. Samples from the bottle and from the closed vessel were transferred to a gas-analysis apparatus already described[13]. In the later experiments, (4) to (7), i.e. those from which the accepted result is derived, the oxygen-content was determined in two stages. First about 99·5 per cent of the oxygen was removed by absorption with solid phosphorus confined over mercury[11], and next the remainder was determined colorimetrically by means of pyrogallol[11]. The accuracy of these methods has already been discussed[11]. The measurements were made in duplicate or triplicate; the error in the figures given in table 6 for the oxygen-content does not exceed 0·1 per cent, and it is considered probable that it may be much smaller than this. In the earlier experiments (1), (2) and (3), the nitrous oxide and oxygen were determined by reduction with excess of carbon monoxide[12] combined with a density-measurement.

On account of the highly oxidizing nature of the products of explosion, the formation of hydrogen or ammonia from water is precluded. For the same reason nitric oxide is absent. A small proportion of nitrogen dioxide ("peroxide") remains unabsorbed by the water in the closed vessel, and thus occurs in the gases in the bottle. It was determined by bubbling an aliquot part of the gas from the bottle†,

* The proportion of nitrous oxide remaining in the closed vessel was higher than that in the bottle, because the decomposition did not propagate past the narrow annulus at the bottom of the head, and also because on the release of the pressure some nitrous oxide which had been dissolved in the 1 ml. of water in the vessel was released.

† This was done immediately after the gas-measurement.

e.g. about 2 litres, through weak hydrogen peroxide acidified with sulphuric acid, and determining the nitric acid so formed by the phenoldisulphonic acid method[14]. The nitrogen dioxide did not exceed 0·3 per cent on the permanent gas.

In view of the lack of any reliable direct chemical method for the determination of nitrous oxide, a physical method is preferred for the determination of this gas. The large proportional difference between the density of nitrous oxide and that of nitrogen or of oxygen makes the measurement of density a suitable method. The densities were measured by the method of direct weighing[12] of the gas, with water vapour and nitrogen dioxide removed, in a glass bulb of approximately 600 cm^3 capacity, a similar bulb containing dry air being used as a counterpoise. The densities were accurate to $\pm 0{\cdot}002$ g. per litre, corresponding to $\pm 0{\cdot}3$ per cent of nitrous oxide in the gas.

Non-gaseous residues in the closed vessel. The closed vessel originally contained 1 cc. of distilled water which absorbed the bulk of the higher oxides of nitrogen. The closed vessel was washed out with distilled water, and an aliquot portion of the washings examined for nitric acid by the Devarda method. In some cases, check tests were made by the phenoldisulphonic acid method. Nitrous acid was shown by Griess tests never to exceed 1·5 mg.

The closed vessel was then opened and washed out with water, and the nitric acid in the washings was determined. Further portions of the washings were tested for iron and for nickel, in order to check whether the walls of the vessel had been attacked by the nitric acid. The iron did not exceed 1 mg. in any case. Nickel was not detected; 0·03 mg. would have been detected.

Checks on analysis. It was considered desirable at this stage to estimate in the final products the ratio of the total nitrogen to the total oxygen. Since the vessel originally contained pure nitrous oxide, any deviation from 2 of this value is a measure of the limit of reliability of the analytical procedure and the extent to which minor reactions, for instance with the walls of the vessel, may occur.

As is shown in table 4, no consistent deviation has occurred, and the magnitude of the deviations observed is within the estimated limits of measurement.

Table 4. Balance of elements

Number of experiment	Quantities of substances present in closed vessel after firing (cm^3 at n.t.p., molecular volumes being taken as 22·40 litres)							Ratio of nitrogen to oxygen
	N_2	O_2	N_2O	N_2O_5	NO_2	Total N (as N_2)	Total O (as O_2)	
1	6089	2958	574	39·1	18	6711	3361	1·997
2	6695	3228	533	48·0	19	7285	3634	2·004
3	7099	3417	521	39·8	4	7662	3781	2·026
4	7108	3459	560	39·1	14	7714	3851	2·003
5	7035	3424	590	26·3	12	7657	3797	2·016
6	6812	3341	633	26·3	22	7482	3746	1·997
7	6659	3273	477	28·0	4	7166	3586	1·998
Mean								2·006

Table 5. Effect of formation of nitric acid and nitrogen peroxide on heat and oxygen

Substance	Reaction	Heat produced (cal.) per mg. of substance	Oxygen absorbed per mg. of substance (cm^3 at n.t.p.)
HNO_3	$2N_2+5O_2+2H_2O=4HNO_3Aq.+59{\cdot}6$ Cal.	0·236	0·45
NO_2	$N_2+2O_2=2NO_2-3{\cdot}4$ Cal.	−0·037	0·49

Table 6. Heat of formation of nitrous oxide

Number of experiment ...	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Estimation of reactant nitrous oxide by measurement of resultant oxygen							
Initial:							
Mass of nitrous oxide (g.)	12·9₆	14·2₅	15·1₁	14·8₈	15·1₃	14·8₂	14·1₆
% oxygen	—	—	—	< 0·01	0·03	0·05	< 0·01
Whence, free oxygen initially present (cm^3 at n.t.p.)	—	—	—	< 1	2	4	< 1
Final:							
Volume of gas measuring bottle (cm^3)	8890	8890	8890	8890	8890	8890	8890
Volume of closed vessel (cm^3)	128	128	128	128	128	128	128
Pressure of gas in bottle and closed vessel (cm. of mercury at 20° C.)	87·26	94·78	100·22	101·36	100·84	98·72	94·62
Temperature (° C.)	19·6	19·4	20·0	21·0	21·6	22·4	20·3
Whence, gas in bottle (cm^3 at n.t.p.)	9488	10310	10883	10970	10894	10635	10262
gas in closed vessel (cm^3 at n.t.p. excluding water vapour)	134	146	154	156	155	151	145
Percentage composition of gas from bottle O_2	30·8	30·9	31·0	31·1	31·0	31·0	31·5
Percentage composition of gas from bottle N_2O	5·8	5·0	4·6	5·0	5·3	5·8	4·4
Percentage composition of gas from bottle N_2	63·4	64·1	64·4	63·9	63·7	63·2	64·1
Percentage composition of gas from closed vessel O_2	27·0	28·5	28·2	30·3	30·1	29·0	27·4
Percentage composition of gas from closed vessel N_2O	18·0	12·5	13·0	7·0	8·2	10·5	17·0
Percentage composition of gas from closed vessel N_2	55·0	59·0	58·8	62·7	61·7	60·5	55·6
Whence free oxygen in bottle and closed vessel (cm^3 at n.t.p.)	2958	3228	3417	3459	3424	3341	3273
Nitric acid in products (g.)	0·220	0·270	0·224	0·220	0·148	0·148	0·157
Nitrogen dioxide in products (g.)	0·037	0·039	0·009	0·028	0·024	0·046	0·009
Whence, Oxygen produced by decomposition of nitrous oxide (cm^3 at n.t.p.)	3075	3368	3522	3572	3503	3431	3430
and, Nitrous oxide decomposed (mol.)	0·274₆	0·300₇	0·314₅	0·318₉	0·312₉	0·306₂	0·298
Measurement of energy							
Temperature rise (° C.)	1·465₅	1·595	1·679	1·707₅	1·672	1·637₅	1·595
Water equivalent (g.)	3767	3771	3771	3771	3767	3771	3771
Whence, total measured heat (cal. ≡ 4·186 joules)	5520	6015	6332	6439	6298	6175	6009
Correction for ignition current (cal.)	12	3	2	9	5	3	1
Correction for nitric acid (cal.)	52	64	53	52	35	35	31
Correction for nitrogen dioxide (cal.)	−1	−1	0	−1	−1	−2	1
Whence, *energy evolved* by decomposition of nitrous oxide (cal.)	5457	5949	6277	6379	6259	6139	5978
Hence, Heat of formation of nitrous oxide at constant volume (cal./mol.)	−19·8₇	−19·7₈	−19·9₅	−20·0₀	−20·0₀	−20·0₁	−19·9

Mean (from experiments 1 to 7) −19·9₅ cal./mol.
(from experiments 4 to 7) −20·0₀ cal./mol.

§ 3. RESULTS

The thermochemistry of the reaction is primarily that of the decomposition of nitrous oxide according to the equation.

$$2N_2O = 2N_2 + O_2.$$

It has been found that side reactions are few. These are limited to the formation of higher oxides of nitrogen and their absorption by water; the corrections applied for the energy and volume changes produced by them have been made in accordance with the constants given in table 5.

Table 6 gives the results of seven successive experiments. Of these, numbers (4) to (7) are considered the more reliable because the oxygen figure was obtained by the direct and accurate method developed for the purpose, and because the general technique had become more familiar; the value $-20{\cdot}0_0$ cal./mol. at constant volume has therefore been derived from these four experiments*.

Table 7. Heat of formation, reactant mass of nitrous oxide being estimated by alternative (less accurate) methods

Number of experiment	Heat of formation (cal./mol.) at constant volume. Mass N_2O estimated from	
	Weight and residual N_2O	N_2 in products
(1)	$-20{\cdot}2_9$	$-19{\cdot}9_1$
(2)	$-19{\cdot}8_3$	$-19{\cdot}7_4$
(3)	$-19{\cdot}6_1$	$-19{\cdot}7_0$
(4)	$-20{\cdot}3_7$	$-19{\cdot}9_7$
(5)	$-19{\cdot}7_1$	$-19{\cdot}8_4$
(6)	$-19{\cdot}8_9$	$-20{\cdot}0_8$
(7)	$-19{\cdot}8_3$	$-19{\cdot}9_9$
Mean	$-19{\cdot}9_3$	$-19{\cdot}8_9$
Mean of (4) to (7)	$-19{\cdot}9_5$	$-19{\cdot}9_7$

The decomposition of nitrous oxide is accompanied by an increase in volume according to the relation $2N_2O \rightarrow 2N_2 + O_2$. The value of the product pressure × volume for nitrous oxide at 42 atmospheres has been found to be 0·67 times that for a perfect gas, as described in part III of this paper. For nitrogen and oxygen, the deviation from the value for a perfect gas is not sufficient to affect the final result by one unit in the dropped figure, and is consequently neglected here. The difference between the heats of formation at constant volume and approximately 42 atmospheres and at constant pressure is found from this data to be 0·48 cal./mol.

The heat of formation at constant pressure is thus $-19{\cdot}5_2$ cal./mol.

* When the accuracy of these measurements was estimated the determination of oxygen was considered an important limit, and it was not relied upon to closer than 0·1 per cent of the total gas, corresponding to 0·06 cal./mol. in the heat of formation. It is not clear how far the higher accuracy attained in experiments (4) to (7) is fortuitous, and how far it may be taken as evidence of the higher accuracy of the oxygen determination.

§ 4. DETERMINATION OF HEAT OF FORMATION BY COMBUSTION METHODS AT PRESSURES OF ABOUT 50 ATMOSPHERES

In the course of these investigations, the combustion in nitrous oxide of hydrogen and carbon monoxide were examined at pressures of about 50 atm., and one of us published an early value[15] obtained for the energy of the former reaction. Values for the heat of formation of nitrous oxide deduced from these two reactions were found however to differ by as much as 1 cal./mol., corresponding to 1 per cent on the measured heats.

A further investigation which was thereupon put in hand showed that thermochemical measurements involving the use of hydrogen in steel vessels at pressures of this order, while likely to give consistent results in any single series of measurements, may be misleading on account of absorption[16, 17] (or in some cases emission) of hydrogen at the walls of the vessel. The behaviour of mild gaseous explosions of this kind is thus similar to what occurs when high explosives are detonated in closed vessels[18]; in the case of the former, however, no effects which exceed 1 per cent of the measured value have been detected. In the estimation of the heat of formation of nitrous oxide in this way, 1 per cent on the measured heat of reaction corresponds with $4\frac{1}{2}$ per cent on the heat of formation, and the method becomes an unsatisfactory one.

The mean figure obtained by using carbon monoxide (table 8) was substantially in agreement with the best results obtained by other methods; the variation between individual determinations was, however, considered unsatisfactory.

Table 8. Heat of formation of nitrous oxide by explosion with carbon monoxide in calorimetric closed vessel. Approximate composition: N_2O, 14 atm.; CO, 24 atm.; N_2, 12 atm.

Measured heat of reaction $N_2O + CO = N_2 + CO_2$	87·2$_2$	86·9$_2$	86·8$_6$	87·2$_8$	87·2$_1$	87·4$_8$	86·7$_4$
Heat of formation of N_2O (cal./mol.) at constant pressure	−19·6$_0$	−19·3$_0$	−19·2$_4$	−19·6$_6$	−19·5$_9$	−19·8$_6$	−19·1$_2$
					Mean	−19·4$_8$	

When nitrous oxide is not present, for instance if oxygen is exploded with excess carbon monoxide[9], a high order of consistency is obtained, and it would seem that the variability is attributable to some action of the former gas. Nitrous oxide was thus found unsuitable as a substitute for oxygen for thermochemical and calorimetric measurements of the kind for which its use had been proposed.

PART III: THE DEVIATION OF NITROUS OXIDE FROM THE SIMPLE GAS LAWS

By T. CARLTON-SUTTON and G. WYN WILLIAMS

The value of the product pressure × volume has been measured for nitrous oxide at pressures of 1 atmosphere and less by Rayleigh[19] and by Batuecas[20]. Values of this product at pressures between 40 and 50 atmospheres were required in connexion with the measurement of the heat of formation of this gas. The method devised for this purpose measures the value of this product in terms of that of a standard gas, and has the advantages that the measurements involved are simple and the apparatus required is such as may be found in any laboratory.

To obtain a check on the general accuracy of this method, the values for carbon dioxide were measured in terms of those for nitrogen and compared with the classical values of Amagat[21], table 9. In view of the agreement thus obtained the method was considered suitable, and the measurements were extended to pressures lower than those employed by Amagat.

Measurements were also made to obtain data for nitrous oxide in terms of those for nitrogen, and from these the deviation of the former gas from the simple gas laws has been deduced.

For any mixture of dry gases, and subject to the restriction that the constituents must act independently in accordance with their partial pressures, the relation between pressure, volume, temperature and mass is given by

$$\Sigma \frac{m}{M} = v \frac{\Sigma \alpha p}{RT},$$

where m is the mass, M the molecular mass and p the partial pressure of each constituent, v is the total volume, T the absolute temperature, R the gas constant, and α the deviation of each gas from Boyle's law expressed as the ratio of the products pv for the perfect and for the actual gas. m, M, p v, T, R α

A strong closed vessel of volume v_1 containing a dry gas X at high pressure p_1, and a large vessel of volume v_2 containing dry air A at a low pressure p_0 are connected and the pressure changes to p_2 when the contents have mixed isothermally. The total mass remains unchanged and the pressure-volume relations may be obtained by equating the two expressions for this quantity, $\Sigma m/M$, which can be derived from the initial and final conditions. v_1 p_1, v_2, p_0 p_2

Initially the mass, $\Sigma m/M$ moles, is

$$\frac{1}{RT}\{{}_X\alpha_1 p_1 v_1 + {}_A\alpha_0 p_0 (g_0 + v_2)\},$$

where the generalized ${}_X\alpha_{1m}$ signifies the deviation of gas X at pressure $(p_1 - p_m)$ and g_n signifies the volume of the gauge and connexions at pressure p_n. ${}_X\alpha_{1m}$ g_n

Finally, when the gases have mixed, the total pressure p_2 is composed of a partial pressure p_3 of air and a partial pressure $(p_2 - p_3)$ of the gas X, where p_3

$${}_A\alpha_3 p_3 / {}_A\alpha_0 p_0 = (g_0 + v_2)/(g_2 + v_1 + v_2).$$

The mass $\Sigma m/M$ moles is then

$$\frac{1}{RT}\{{}_x\alpha_{23}(p_2-p_3)+{}_A\alpha_3 p_3\}(v_1+v_2+g_2),$$

which $$=\frac{1}{RT}\left\{{}_x\alpha_{23}\left[(p_2-p_0)(v_1+v_2+g_2)+p_0v_1+p_0(g_2-g_0)+p_0(v_2+g_0)\left(1-\frac{{}_A\alpha_0}{{}_A\alpha_3}\right)\right]+{}_A\alpha_0p_0(g_0+v_2)\right\}.$$

Equating these two expressions for $\Sigma m/M$ we find that

$$p_1\frac{{}_x\alpha_1}{{}_x\alpha_{23}}=(p_2-p_0)\frac{v_1+v_2+g_2}{v_1}+p_0+p_0\frac{g_2-g_0}{v_1}+p_0\frac{v_2+g_0}{v_1}\cdot\frac{{}_A\alpha_3-{}_A\alpha_0}{{}_A\alpha_3}\quad\ldots\ldots(1).$$

In a practical case when $p_2=1/3$ atm., $p_0=1/300$ atm., $v_1=128$ cm^3, $v_2=16$ litres, and $(g_2-g_0)=1$ cm^3, the second term on the right is less than 0·01 per cent of the first term and the remaining terms are still smaller. For such cases, therefore, all terms but the first may be neglected.

If there is no diffusion of air from the large vessel to the strong closed vessel, the final value of $\Sigma m/M$ may be written

$$\frac{1}{RT}\{{}_x\alpha_{20}(p_2-p_0)v_1+{}_x\alpha_0p_0v_1+{}_x\alpha_{20}(p_2-p_0)(g_2+v_2)+{}_A\alpha_0p_0(g_2+v_2)\}$$

and equation (1) becomes

$$p_1\frac{{}_x\alpha_1}{{}_x\alpha_{20}}=(p_2-p_0)\frac{v_1+v_2+g_2}{v_1}+p_0\frac{{}_x\alpha_0}{{}_x\alpha_{20}}+p_0\frac{g_2-g_0}{v_1}\cdot\frac{{}_A\alpha_0}{{}_A\alpha_{20}}.$$

For this expression, also, all terms but the first may be neglected. In practice, ${}_x\alpha_{20}$ and ${}_x\alpha_{23}$ are to a high order of accuracy equal, and the two expressions consequently become the same. The final values obtained by this method, therefore, are not affected by the amount of diffusion that takes place.

The simple relation obtained by neglecting the small terms in equation (1) involves two pressures p_2 and p_0 which can be measured on an open mercury manometer, and one pressure p_1 which is too great to be measured conveniently in this way. To compare the values of ${}_x\alpha_1/{}_x\alpha_{23}$ with the corresponding values for a standard gas, however, no measurement of this pressure p_1 is required, since if the pressure can be reproduced (without measurement) in two experiments, the relation becomes

$$\frac{{}_x\alpha_1}{{}_x\alpha_{23}}\Big/\frac{{}_x\alpha_1'}{{}_x\alpha_{23}'}=\frac{p_2-p_0}{p_2'-p_0'}\cdot\frac{v_1+v_2+g_2}{v_1+v_2+g_2'}\quad\ldots\ldots(2),$$

where the dashes denote that the quantities refer to the standard gas.

The differences between g_2 and g_2' have not exceeded $v_2\times10^{-4}$, and the second factor on the right-hand side has consequently been taken as unity.

With considerable accuracy, therefore, ${}_x\alpha_1/{}_x\alpha_{23}$, the ratio of the deviations at pressures p_1 and (p_2-p_3) respectively, is directly proportional to the measured rise in pressure in the small vessel. When, as in the present cases, the deviation ${}_x\alpha_{23}$ at low pressure is known, the deviation ${}_x\alpha_1$ at any pressure p_1 can be measured in this way.

Table 9

Volume v_1 of small vessel = 128 cm³ Volume v_2 of bottle = 16·46 litres (except in experiments *A* and *K* for which v_2 = 15·35 litres)											
Experiments in chronological order...	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*K*	*L*	*M*
Temperature of small vessel... ...	19·6	20·0	19·3	20·1	19·4	19·7	19·0	19·1	18·9	19·1	19·7
Pressure-rise, $p_2 - p_0$ (cm.) in bottle in experiments with											
nitrogen (i) and (v)	12·64	14·62	20·52	17·68	26·29	25·70	23·48	20·59	29·00	5·97	6·99
carbon dioxide (ii) and (iv)	14·26	17·05	26·21	21·43	37·79	36·38	32·03	26·49	41·99	—	7·44
nitrous oxide (iii)	14·44	17·37	26·86	22·00	40·41	38·39	33·11	27·23	45·44	6·37	7·55
Pressure p_1 (atm.) in small vessel											
indicated approximately on aneroid gauge	20	25	35	30	45	44	40	35	46	10	11
derived from the measurements with nitrogen	19·8	24·6	34·5	29·7	44·0	43·1	39·4	34·5	45·4	10·1	11·8
Values of α_1/α_{23} for											
nitrogen[5]	1·006	1·007	1·008	1·008	1·010	1·010	1·009	1·008	1·010	1·003	1·004
carbon dioxide	$1·13_4$	$1·17_3$	$1·28_8$	$1·22_5$	$1·45_4$	$1·42_5$	$1·37_6$	$1·29_9$	$1·45_6$	—	$1·06_7$
nitrous oxide	$1·14_8$	$1·19_4$	$1·31_1$	$1·25_4$	$1·55_1$	$1·50_4$	$1·42_3$	$1·33_5$	$1·57_9$	$1·07_3$	$1·08_4$
Value of α_{23}											
for carbon dioxide[5]	1·001	1·002	1·002	1·002	1·003	1·003	1·003	1·002	1·004	—	1·001
for nitrous oxide[5, 6]	1·002	1·002	1·003	1·002	1·005	1·004	1·004	1·003	1·005	1·001	1·001
α as deduced at above temperatures and pressures											
for carbon dioxide	$1·13_5$	$1·17_5$	$1·29_1$	$1·22_7$	$1·45_8$	$1·42_9$	$1·38_9$	$1·30_1$	$1·46_3$	—	$1·06_8$
for nitrous oxide	$1·15_0$	$1·19_6$	$1·31_5$	$1·25_8$	$1·55_9$	$1·51_0$	$1·42_9$	$1·33_9$	$1·58_7$	$1·07_4$	$1·08_5$
α (Amagat) for carbon dioxide	—	—	—	—	$1·45_0$	$1·43_2$	$1·36_9$	—	$1·48_3$	—	—
Ratio pv actual/pv perfect											
for carbon dioxide	$0·88_1$	$0·85_4$	$0·77_5$	$0·81_5$	$0·68_6$	$0·70_0$	$0·72_5$	$0·76_9$	$0·68_4$	—	$0·93_6$
for nitrous oxide	$0·87_0$	$0·83_6$	$0·76_1$	$0·79_5$	$0·64_1$	$0·66_2$	$0·70_0$	$0·74_7$	$0·63_0$	$0·93_1$	$0·92_1$

It is to be noted that equation (2) does not involve p_1, the initial pressure in the large vessel. In practice, this pressure has been adjusted so as to be the same for the gas under test as for the standard gas; it has not been necessary to measure it directly since the condensation of the standard gas at pressure p_1 is given by the expression ${}_1\alpha_{23}'(p_2'-p_3')\,v_2/v_1$, and from the known properties of this gas the corresponding value of p_1 can be obtained.

To meet these requirements the following apparatus has been used: A strong closed vessel v_1 of capacity 128 cc., designed for use in the calorimetry of propellants; a large bottle v_2 of capacity 16 litres, which had been carefully calibrated for measurement of the volumes of the gaseous products of explosives; a mercury manometer for the measurement of the pressures, p_0 and p_2, less than one atmosphere; and an aneroid gauge which, while not measuring the pressure, enabled the vessel v_1 to be filled to the same initial pressure in each of a series of experiments.

A complete series consisted of five experiments in which (i) nitrogen, (ii) carbon dioxide, (iii) nitrous oxide, (iv) carbon dioxide and (v) nitrogen were used successively. Agreement between the first and fifth and the second and fourth experiments has been taken as a sign that the indications of the gauge were satisfactory throughout the series. The results are given in table 9.

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DEMONSTRATION

621.318.5

A RELAY FOR OPERATING TWO CIRCUITS ALTERNATELY WITH DELAYED ACTION

by D. S. PERFECT, M.A., D.Phil., National Physical Laboratory

Demonstration given on February 15, 1935

THIS relay was designed to perform in a regular cycle the tilting of a mirror backwards and forwards in order to throw radiation on and off a thermopile. The action is delayed for a definite interval of time after the giving of a warning signal, to enable the observer to take the indication of the thermopile at a particular moment before the change-over occurs. Certain features of the design may have a wider interest, since there are several applications in which an alternately acting arrangement is useful with or without delayed action, and this particular instrument has the merit of cheap and simple construction, so that almost anyone could make it for himself.

The general arrangement is shown in figure 1, and certain components in more detail in figures 2, 3 and 4. The details of wiring are omitted as they are fairly obvious and would confuse the diagrams.

M is a synchronous (gramophone) motor run off the 50-cycle, 100-volt mains, and adapted by the addition of the ebonite drum *d*, and gearing which causes the drum to rotate about a vertical axis at one revolution per second. Let into the surface of the drum is a vertical strip of brass which at every revolution makes electrical contact between two horizontal strips of phosphor bronze sprung into contact with the drum. The dry cell B_1 is thus made to give an impulse every second to the clock *C* which has a synchronome movement. At the circumference of what would normally be the dial is an annulus *r* of keramot into which five equally spaced segments of brass are inserted. The internal surface of the short cylindrical tube formed by the annulus is turned in the lathe so that the brass segments are exactly flush with the surface. The segments are in mutual electric connexion. At the end of the hand *h* is sprung a platinum contact piece which presses against the internal surface of the annulus and follows behind the hand. Thus every 12 seconds for the duration of a second an electric path is opened between the contact piece and one of the brass segments, and a circuit of which these are part is completed.

If the clock had been specially made for the purpose in view it would have been easy to arrange the segments in two sets spaced alternately, so that alternate circuits could be completed which should operate the desired mechanism through a simple type of relay. A relay of some kind is necessary because the power required to operate the final mechanism is greater than could be passed directly through the clock without causing destructive sparking. But in point of fact the clock, as also the synchronous motor, was already in use to give simple warning signals every 12 seconds, and thus these two elements were available, in the form

described above, when the details of the method for producing alternate action were in question.

When the circuit through the clock is completed, the dry cell B_2 operates in parallel the buzzer Z and the electromagnet m. The magnet m (see also figure 2)

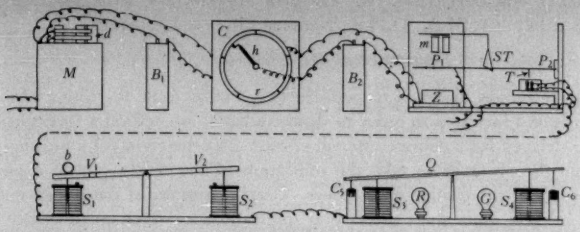

Figure 1.

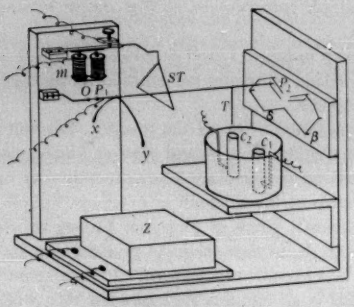

Figure 2.

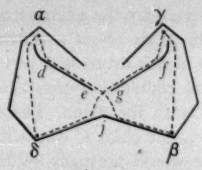

Figure 3

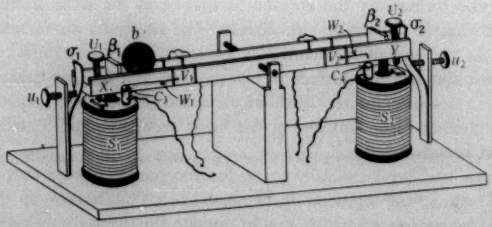

Figure 4.

is part of an electric bell adapted by having a wire stirrup ST soldered to the end of the striking arm in place of the ball. A light rod P_1P_2, consisting of a piece of steel wire about 20 cm. long and 1 mm. in diameter, is constrained at P_1 by a short length (about 1 mm.) of thread attached to it and to the end of a fixed piece of

thick wire O with sealing-wax. It is constrained by its weight to rest in contact with the horizontal portion of the stirrup ST (the point of contact being about 4 cm. from the end P_1) and about its longitudinal axis by the action of a wire xy fastened to it by sealing wax near the end P_1. The centre of gravity of the wire is between P_1P_2 and y so that the end x is kept pressed against the vertical face of the wooden upright that holds O and m. Thus the short wire T, which depends from the rod near the end P_2, is kept approximately vertical. The rod is also constrained near the end P_2 by a system of wires shown in greater detail in figure 3 which is roughly to scale. The system of wires was actually made by inserting ordinary pins into a block of wood and suitably bending them. The range of vertical movement of the stirrup is such that at one extremity the stirrup presses the rod so that the end P_2 is forced into either of the corners α, γ, and at the other extremity leaves it free to rest under gravity in contact with either of the corners β, δ. There are thus four positions of rest which the rod can take up, but the pins are arranged so that these must be reached in a definite cyclic order, namely $\alpha\beta\gamma\delta$, the path of P_2 being shown by the dotted line. For suppose that initially P_2 is at α. When m receives an impulse the stirrup is depressed and the rod falls till it strikes the pin de. It slides down the pin till it reaches the end e when it slips through the gap between e and g. It would now be geometrically possible for it to proceed either to δ or β, but its path is in fact determined mechanically, for in virtue of its horizontal momentum it continues to travel to the right, and by the time it has fallen sufficiently to reach the constraining pins again it is definitely to the right of the dividing edge j and therefore slides down the pin $j\beta$ till it is brought to rest at the corner β. The current supplied to m by the clock lasts for one second, whereas the time taken for the rod to pass from α to β is only a fraction of this. The rod therefore rests at β for the best part of a second. Then the current in m ceases, and the stirrup springs vertically upwards carrying the rod with it. The end P_2 has no choice but to follow a course such as the dotted line till it is brought to rest by the corner γ, where it stays till the next impulse is given by the clock 12 seconds later. It then proceeds in a similar way from γ to δ and thence back to the starting point α. Two mercury cups c_1, c_2, figure 2, are arranged so that when P_2 is at β or δ the wire T is dipping into the corresponding cup. These cups are of glass: each has a T tube of small diameter attached near the bottom and bent upwards. Into the mercury contained in these T tubes iron wires are inserted to make electric connexion. The cups are contained in a cylindrical glass jar which is kept full of distilled water so as completely to submerge them. This arrangement was found to be satisfactory in damping sparks and keeping the mercury clean. It is in this respect far preferable to immersion in oil. The only trouble that arises is that a small quantity of the mercury is atomised by the spark every time the circuit is broken, but this mercury merely collects at the bottom of the jar, and all that is required to maintain the arrangement in working order is the occasional addition of a little mercury to the cups, and of course the periodical addition of distilled water to the jar. The jar rests on a shelf which can be clamped to the wooden upright at the height necessary for correct adjustment of the mercury

cups relative to the wire T. The rod P_1P_2 (by means of a wire attached near the jointed end P_1) and the mercury cups are in circuits (connected through suitable resistance to the 100-volt d.c. mains) which operate one or other of the solenoids S_1, S_2 of figure 4, which shows the arrangement for delayed action. A wooden bar XY is pivoted about its centre. The range of its possible rotation is defined by the adjustable screws U_1, U_2, the ends of which come up against small brass blocks screwed to the upper faces of the solenoid bobbins. The strip springs σ_1, σ_2 press against the ends of the bar by an amount which can be adjusted by the screws u_1, u_2, so that the bar just does not slip under the weight of the ball b. Attached to the sides of the bar are two strips of brass the upper edges of which are milled so as to be flat and parallel. They are sawn through in four places so as to give two electrically isolated sections V_1, V_2. The gaps are filled in with ebonite so that the top edges are mechanically continuous.

Suspended by hooks screwed into the under surface of the bar, two iron rods hang inside the bobbins of the solenoids S_1, S_2, which are waxed to the base in such positions that the rods hang freely. The solenoids consist of 1-lb. reels of 24 s.w.g. copper wire as commercially supplied. Successive impulses given to the solenoids by the operation of the relay give successive pulls to the iron rods and tilt the bar backwards and forwards. A 1-in. steel Hoffmann ball b rests between the brass rails described above and rolls between two wooden blocks β_1, β_2 which are fixed near the ends in front of the screws U_1, U_2 and act as buffers. The limits of tilt of the bar are adjusted by the screws U_1, U_2 so that the ball, starting from rest at either end, takes the required time, after the impulse is given to the bar, to reach the insulated section at the other end. The sections V_1, V_2 are connected respectively to two solenoids, S_3, S_4, figure 1, similar to S_1, S_2 and in circuit with the 100-volt mains so that as the ball on its journey from X to Y passes over V_2 it operates the solenoid S_4. Before reaching V_2 however, the ball must pass the section V_1, and this would give an impulse to S_3, but as S_3 was the last to be operated in the previous cycle this additional impulse would cause no reversal. Nevertheless in order to save the total amount of sparking at the rails, and also to eliminate magnetic disturbances which were otherwise set up, and were objectionable for the particular purpose in view, an arrangement was made automatically to cut out this additional impulse. Mercury cups C_3, C_4, figure 4, are attached to the tops of the bobbins S_1, S_2 respectively, and wires W_1, W_2 are attached to one side of V_1, V_2 respectively, and form parts of the corresponding circuits. The wires are adjusted so that when the end X moves down, W_1 dips into C_3 and W_2 is withdrawn from C_4, and when the end X moves up, W_1 is withdrawn from C_3 and W_2 is inserted in C_4. Thus when the end X is down, V_1 is in circuit, but when S_2 tilts the bar this disconnects V_1 before the ball has time to reach it, but puts V_2 in circuit in plenty of time. Sparking at V_1, V_2 is reduced by connecting a condenser across each. Merely for the purpose of demonstrating the working of the system, the solenoids S_3, S_4 were made to tilt backwards and forwards a brass rod Q, figure 1, which made alternate contacts at the mercury cups C_5, C_6, and lit up alternately a red lamp R and a green lamp G. In the arrangement for which

the relay was designed a rod that is operated in a similar way to Q (but without any further circuits being involved) works the mechanism referred to in the opening section. In conclusion I should like to thank my colleague, Mr J. Guild, for his interest and assistance in discussing the design at various stages.

Note added November 18, 1935

Since the relay was demonstrated in the form described above, the details of construction of the portion which gives delayed action have been somewhat modified.

It was found that the gradual pitting of the surface of the ball which resulted from sparking eventually caused the ball to be retained in its position of rest at the extremity of the bar when the tilt of the bar should have caused it to begin rolling. This was not a very serious trouble since a new ball is easily substituted for the old. But in addition the pitting of the live section of the rail, particularly at the ends of the section where the ebonite is inserted in the gaps, caused the ball to be held up at these points. To remedy this a new bar was made, the rails of which are continuous steel strips. Between the rails at each region corresponding to an insulated section in the previous arrangement is placed a pair of light steel strip springs with platinum contacts at the ends. The springs are one above the other, so that in passing over them the ball presses the top spring on to the one below and closes the circuit at the platinum contact. The ball and the rails should thus last indefinitely, and the platinum contacts can at any time easily be renewed.

REVIEWS

Probability and Random Errors, by W. N. Bond. Pp. viii+141. (London: Edward Arnold and Co., 1935.) 10*s.* 6*d.*

Probability, especially in its application to the theory of errors and the reduction of observations, is as prolific a source of argument and debate as any other branch of philosophy. It would be easy to spend a pleasant evening by the fireside disputing some of the views expressed in this book—or equally pleasant, if one's companion preferred the role of attacker, to pass the hours in defending them.

Point one, to which the debate would frequently return, would be the question whether subsequent knowledge of a more accurate result can be a reason for supposing that one method of treatment of earlier, less accurate, data is better or worse than another treatment. The protagonists would also have the opportunity for a fine clash over the question whether the advice given seventy years ago to astronomers, to help them to decide which observations of parallax (many of which were smaller than their probable errors) ought to be rejected, is of general application. Doubtless, neither side would convert the other but, what is more important, the defender of the book would not at any stage have to repudiate his text.

It can truthfully be said that any readers who contemplate either debating the theory of errors in general or using the methods in reducing observations should certainly be familiar with the contents of this book. Admittedly, it would be well if they were familiar with more, since it is only a ground-work. Within that limitation, however, it is sound and accurate. Among the omitted matters, which might be considered for inclusion in the next edition, are the method of fitting a curve to observations when both coordinates of each point are uncertain, and some sketch of the recent work on goodness of fit.

J. H. A.

A Table of Eisenstein-Reduced Positive Ternary Quadratic Forms of Determinant < 200, by Burton W. Jones. 51 pp. (*Bulletin of the National Research Council*, No. 97. Washington, 1935.) $1.00.

In connexion with the theory of numbers, quadratic forms

$$ax^2+by^2+cz^2+2ryz+2szx+2txy$$

are of interest. Although it is true that by substitutions of the type $X=\alpha_1 x+\beta_1 y+\gamma_1 z$, such a form can in general be transformed into any other quadratic ternary form, yet if the coefficients of the substitution are restricted to be integers, and its determinant $|\alpha_1\beta_2\gamma_3|$ to be unity, then the variety of transforms is limited. Of all forms obtainable by such a restricted transformation from a given form, one can be selected as the representative. Eisenstein has shown how to select this reduced form uniquely, and the present table shows the type-forms corresponding to any given form.

Since the determinant of the transformations considered is unity, the determinant

$$\begin{vmatrix} a & t & s \\ t & b & r \\ s & r & c \end{vmatrix}$$

of the form itself is unaltered by the substitution. Thus the basis of the classification is the determinant of the form. For each value of this determinant from 1 to 200, the table shows the values of a, b, c, r, s, and t in the equivalent forms. There may be as many

as 59 of these reduced forms for a given determinant, and the coefficients for each of the 59 are in such a case given separately. In addition, the actual number of these sub-cases is stated, as well as the number of *automorphs* of each reduced form. (The automorphs of a form are the forms obtained by transformations which turn the form into itself, i.e. the number of automorphs in effect shows the degree of arbitrariness in the actual substitution needed to effect the desired transformation.)

No method is suggested whereby the sub-class can be determined to which a given form belongs, nor is any *process* offered for finding the transformation from a given form to its appropriate reduced form. This is not really necessary, since the purposes for which these forms are used only require that the properties of the reduced form be known. The reduced form is in fact so far representative of all its equivalents, that the properties of both are identical in so far as the applications to number theory are concerned. For this purpose, the present table is admirable. It is more extensive than any precursor, is very clearly arranged, well printed and inexpensive. J. H. A.

Der Aufbau der Atomkerne (*Natürliche und Künstliche Kernumwandlungen*), by L. MERTNER and M. DELBRÜCK. Pp. ii+62. (Berlin: Julius Springer, 1935.) RM. 4.50. (Paper cover.)

This is an attractive little book, which can be especially recommended to honours students as an introduction to the study of nuclear physics, and as material for practice in reading German. The first part deals with experimental results, the second with their interpretation in terms of quantum mechanics. The treatment is non-mathematical.

H. R. R.

The Structure of Metallic Coatings, Films and Surfaces. The Sixty-second General Discussion of the Faraday Society, March, 1935. Pp. 248, and 77 plates. (London: Gurney and Jackson, 1935.) 21*s.* net.

It would be superfluous to emphasize here the value of the discussions held periodically by the Faraday Society on physical and chemical subjects. The high prestige that they have attained in the view of all physicists and chemists as a source of accurate and up-to-date information on many varied topics is a sure guide to their utility. The discussion under review is no exception. Indeed, owing to its practical nature and an almost unique blending of pure and applied science, it is likely to be of even wider interest than many of the previous discussions.

The first half of the discussion, on electron-diffraction, will prove of great value to all those interested in this modern development of physics, which, by reason of the results already obtained, may be placed with microscopy as one of the most powerful methods of research available to the metallographer in the study of metal surfaces. Indeed, it is perhaps surprising that a development of such practical importance should have arisen so directly out of the abstruse physical theories of de Broglie. Prof. Finch's complete and beautifully illustrated paper provides an excellent introduction to the method and its applications, while the other papers on this subject also provide material of importance to both physicists and metallographers. Of particular interest is the evidence given by electron-diffraction in favour of Beilby's theory of an amorphous layer on the surface of polished metals.

The second part of the discussion, on metallic coatings, affords a very comprehensive survey of the methods of investigation which may be applied to metal surfaces, in particular to electrodeposited coatings. Optical methods are the subject of two interesting papers by Dr Tronstad and Prof. Ornstein respectively, while others illustrate the metal-

lurgical and X-ray methods of examination. The other papers deal with almost all aspects of electrodeposition in a manner which will doubtless be of interest to both electrochemists and electrodepositors. Finally there are two papers on the formation of coatings by spraying and dipping respectively. It is to be hoped that this discussion will stimulate scientific as against the hitherto rather empirical methods of attacking the problems associated with the production of metallic coatings by electrodeposition and other methods.

No review of this book would be complete without reference to the seventy-seven plates, of which almost half are electron-diffraction photographs. The reproductions are excellent, as indeed is the whole production of the book. S. F.

The Structure of Crystals. Supplement for 1930–4 to the second edition, by RALPH W. G. WYCKOFF. 240 pp. (American Chemical Society Monograph Series: Reinold Publishing Corporation.) $6.00

Dr Wyckoff's earlier volume contained descriptions of determinations of X-ray structure made previous to and during the year 1930. This supplement continues the account up to the year 1934. Some idea of its scope may be gained by noting that the index of substances contains over 1000 entries, and the bibliography a list of over 2000 papers.

Now that such complex structures are being analysed, the best method of presenting the results in the form of figures is a serious problem. The author gives in most cases a plan of the structure with an indication of the heights of the atoms above the plane of projection, and an accompanying sketch to this same scale in which the atoms are shown as shaded spheres packed together. This scheme is very successful and enables the nature of the structure to be grasped easily.

The Structure of Crystals is one of the essential books of reference for all who work in this field of X-ray analysis, or who need information about crystalline structure. The labour of compiling such a work is great, because authors have many different ways of stating the results of analysis, and each paper must be thoroughly mastered before its contents can be paraphrased into a common conventional form such as is used in the book. We owe a debt of gratitude to Dr Wyckoff for bringing his work up-to-date and so materially assisting the progress of research. W. L. B.

Infra-red and Raman Spectra, by G. B. B. M. SUTHERLAND, M.A., Ph.D. Pp. xi+112. (Methuen's Monographs on Physical Subjects. London: Methuen and Co., 1935.) 3*s.* net.

Though of comparatively recent growth; the two branches of spectroscopy surveyed in this monograph have become so extensive and have assumed such importance in the investigation of the structures of the ground states of polyatomic molecules that each of them needs a considerably larger monograph to itself. Compactness, however, is an avowed and laudable object of this well-known series. In order to condense the essentials of both into 112 small octavo pages, the author treats them as a means of investigation of molecular structure rather than as subjects in themselves. For readers interested in other aspects of these spectra, however, the monograph will be helpful as an introduction. The opening chapter deals with experimental methods, the second chapter with the normal vibrations of molecules of several different types, the next two chapters with non-electronic infra-red absorption bands, i.e. vibration-rotation bands and the far infra-red rotation bands, and the fifth and last chapter with the correlation of these bands and Raman spectra. A bibliography is provided, in addition to references at the end of each chapter. The appendix contains numerical values of internuclear distances, moments of inertia and vibrational frequencies of some molecules in their ground states, as determined from analysis of these spectra. W. J.

Veröffentlichungen des Wissenschaftlichen Zentral-Laboratoriums der Photographischen Abteilung-Agfa. Band IV. Pp. vi + 262. (Leipzig: S. Hirzel, 1935.) RM. 12.50.

The Agfa Company is fortunate in possessing an enthusiastic band of research workers, and the present volume, forming No. 4 of the series of collected papers, contains a number of articles contributed on the occasion of the International Congress for Applied Photography held in Paris this year (1935).

The volume appears to convey a very good idea of the contemporary state of photographic research. We notice papers dealing inter alia with the present theories of the latent image, the measurement of the granularity of developed films, photographic plates for scientific photography, grid lenses, the use of Scheiner disks in Röntgen-ray sensitometry, the resolving-power of photographic objectives, and the kinematographic reproduction of the sensation of space.

It would be quite impossible to deal with more than a small fraction of these topics except in a very long review, but it may be useful to many to know that while perhaps the majority of the articles are addressed to photographic research workers and photographic specialists, there are a number of sections, such as H. K. Weichmann's article on photographic plates for scientific photography which will be of the greatest interest to spectroscopists, microscopists and many others. The spectral sensitivity of various Agfa emulsions is described both verbally and with the aid of step-exposure spectrograms. Both ultra-violet and infra-red plates are described, and the appropriate methods for super-sensitizing the infra-red plates are discussed. The plates described here can be compared with the Ilford products of which short particulars are given in the *Journal of Scientific Instruments* for October, 1935 (p. 333).

Opticians, too, will be interested in Kujawa's article on the resolving-power of photographic objectives in which an interesting attempt is made to develop a method of comparing the relative sharpness of images given by various objectives in a manner really related to the proper conditions of performance. Only too often the results obtained with lens-testing benches can be misinterpreted, and the evolution of a really good test is much to be desired.

The volume is very attractively printed and well illustrated with clear diagrams and photographs. L. C. M.

Elements of Loud-Speaker Practice, by N. W. McLachlan. Pp. viii + 160. (Humphrey Milford: The Oxford University Press, 1935.) 5*s.* net.

If the extent to which an author achieves his purpose is a measure of the success of his book, then Dr McLachlan, who aims at telling "the average person, (1) the purpose of a loud-speaker, (2) how it works, (3) how it is designed, and (4) the effect of the room where it is used upon the sound reproduction", is to be congratulated upon the result of another journalistic venture. The text, which, with the exception of a chapter on recent developments, is derived from a series of articles published in *World Radio* during the latter half of 1933, deals not only with the various forms of loud-speaker but such cognate subjects as baffles and the coupling of the loud-speaker with the power valve. The treatment is authoritative and non-mathematical; the analogies employed are kept within the bounds of the elastic limit; and as the diagrams are as clear as the arguments are lucid the volume, which is well produced and a handbook in the non-teutonic sense, is suitable for relieving the tedium of a train journey. The book should do much to dispel the mist of mixed and doubtful notions with which its subject is apt to be surrounded, and may be recommended both to the "average person" and to those wishing to perceive the loud-speaker wood in true perspective in preparation for a detailed study of any particular tree. E. J. I.

Noise, by N. W. McLachlan. Pp. vi+148. (Humphrey Milford: The Oxford University Press, 1935.) 6*s*. net.

As author of this readable little volume Dr McLachlan appears again in his now familiar role of pioneer and provides us with what we believe to be the first book to be published in this country on the subject of noise. The matter is treated from a general rather than a technical standpoint, and the book, dealing as it does with the behaviour of the ear, the measurement of noise and frequency analysis, the noise encountered in various locations and the agencies which produce it, as well as with the physiological and psychological effects of noise and its mitigation, justifies its claim to be a comprehensive survey from every point of view. Although in consequence the book is of the nature of a compilation, the diverse matter it reports—gleaned from some hundred and forty sources cited in an appendix—has been sifted and welded into a well-knit whole. A feature of the text is the use of the expression "reftone level" which conveniently connotes in decibels "the intensity level of the equally loud reference tone of 1000 c./sec. above the datum or threshold of 200 microdynes per cm^2." The volume is a companion one to the author's *Elements of Loud-Speaker Practice*, and, to paraphrase Sir Henry Fowler's foreword, the book should prove invaluable to those actually interested in the subject as well as to the ordinary man upon whom it is forced. E. J. I.

Anecdotal History of the Science of Sound, by D. C. Miller, D.Sc., LL.D. Pp. xii+114. (London and New York: Macmillan Co., 1935.) 10*s*. 6*d*. net.

The author deplores the lack of information on the history of sound given in the text-books, citing two well-known histories of physics in English from which the subject is almost completely omitted. Although we think he would revise his statement if he referred to standard German histories, such as that of Hoppe, it is undoubtedly true that this branch of study was passed over by the majority of physicists until the last few years. No better proof of this statement could be given than the fact that in this country Prof. Miller is more widely known for his ether-drift experiments than for his, probably more extensive, work on the sounds produced by musical instruments.

The book is an attempt to stop this gap in scientific history. It would be unfair to criticize it as a historical treatise, since the author disclaims the intention to write one. The book does in fact give a series of detached notes on the lives and work of experimenters in sound from Pythagoras to W. C. Sabine, i.e. in what one might call, for want of a better classification, pre-War acoustics. It is curious that until the middle of the last century work in sound was almost entirely in the hands of musicians and mathematicians, so that practice and theory pursued separate paths for a longer period than in any other branch of science, except possibly the sister science of hydrodynamics.

The reader of a book like this inevitably finds that his cherished opinions disagree at times with those of the author. For instance, the statement "the flute is the simplest of wind instruments, yet one cannot by theoretical calculation locate any finger-hole on a flute tube which will produce a given tone" is hardly fair to recent applications of Webster's concept of acoustic impedance, while the summing-up of Rayleigh's work in the words "Of discoveries sensationally new there is perhaps not one to record, though his experiments have justified many theoretical conclusions and have suggested new points of view" seems rather faint praise of a great scientist. Nevertheless the book is very readable and inspiring, and will undoubtedly form the basis of an historical treatise on sound for whoever is willing to undertake the task of writing one. E. G. R.

Physics for College Students, by A. A. KNOWLTON, Ph.D., Professor of Physics, Reed College. Second edition. Pp. xxi + 623. (McGraw-Hill Publishing Co., 1935.) 21*s.* net.

This is an exceptional book in virtue of the general line of treatment adopted by the author, who is an enthusiastic and successful teacher. It is a noteworthy example of an effort to humanize the subject, by breaking away from the beaten track that has been followed by successions of teachers and pupils whose gaze is turned oft and anon upon examination requirements, and by seeking rather to reveal the wealth of the subject-matter, attained often by heroic human achievement, and very relevant to the enjoyment of a full life of action and thought.

The course is intended to occupy a year, and to be taken both by those who do and those who do not intend to pursue the subject of physics further during their college career. This is the second edition of the book, and in the intervening seven years the author, while adhering to his main principle of treatment, has made improvements in selection of material and in simplification here and there, as experience has dictated.

One is struck at once by the absence of the usual segregation of phenomena into the classes mechanics, heat, light, etc., and the idea of a unification soon begins to take shape. Energy occupies a commanding place, and branches, such as radio-electricity, which have recently risen to special importance on account of their attractive applications, or which, like cosmic rays, have made widespread appeal to intellectual curiosity, are given a substantial place.

The mathematical treatment is of the simplest, no mathematics more difficult than simple algebra and trigonometry being drawn upon. Formulae appear in plenty, often without more than a suggestion of the line of proof, but they are clearly explained and applied. Though no previous knowledge of physics is assumed on his part, the student finds his attention directed to a vast array of topics which may be of the usual homely type, such as thermometers, lenses, sound waves, the earth's magnetism, Ohm's law, and so on; or which may belong to categories usually considered abstruse, and outside the range of the elementary student, such as Bernoulli's theorem, the diffraction of light, elliptic polarization, the Michelson-Morley experiment and the theory of relativity, the equivalence of mass and energy, the quantum of radiation and Planck's constant, and many more. Teachers would do well to read this book, and to see how it is possible to create real intellectual interest and to impart a useful body of knowledge in a field so vast as that of the physics of to-day.

The book is plentifully illustrated with diagrams and photographs, with one coloured plate showing spectra, and the whole is excellently produced. D. O.

Introduction to Physical Science, by CARL W. MILLER. Second Edition. Pp. xiv + 409. (Chapman and Hall.) 15*s.* net

Prof. Miller emphasizes the close relationships between the classical divisions of physics—heat, light, sound and electricity—and leads the student gradually and easily "with no mathematics beyond that common in high school courses" to the study and appreciation of such modern subjects as relativity, artificial atomic disintegration, wave mechanics and cosmic physics. The atom and the elementary particles really do get plenty of notice but molecular phenomena are somewhat overlooked; for instance, surface tension is not mentioned. This rather great emphasis on atomic physics would seem to be unfortunate in a book of this standard and generality and with this title.

The aim of the author has been "to lead the student by as natural steps as possible

from the beginnings of scientific thought through to the surprising results of modern research" apparently "in the short space of a single year".

Such ambition merited success and this early publication of a second, somewhat enlarged, edition is an indication that a measure of success has been achieved. J. H. B.

Le Pansoma et la Géométrie de l'Énergie, by Dr A. C. Léeman. Pp. viii+257. (Genève: Georg et Cie. S.A. Libraires-Editeurs, Librairie de l'Université, 1935.) Fr. 15.

This book is quite harmless. It contains a large variety of rather feeble speculations which have as their object the unification of recent advances in modern physics, geometry, biology and psychology by the use of the concept of the Pansoma. The author's investigations seem to have no point of contact with the real world and to be exclusively occupied with verbal and numerical jugglery. G. T.

Pareto's General Sociology. A Physiologist's Interpretation, by Lawrence J. Henderson. 119 pp. (Cambridge Harvard University Press. London: Humphrey Milford, Oxford University Press, 1935.) 5*s*. 6*d*. net.

This little book, one half of which is occupied by notes on the text, has been written to provide an introduction to the treatise on General Sociology by Prof. V. Pareto of the University of Lausanne. According to the author, Pareto's researches in sociology have been profoundly influenced by Machiavelli's pioneer study entitled *The Prince*.

This work has a certain interest for students of chemistry and physics inasmuch as the general concept of a physico-chemical system in thermo-dynamical equilibrium is used as an analogy illustrative of Pareto's concept of a general social system; but the analogy is only sketched and, doubtless for very good reasons, receives no systematic development. Pareto's work has already had a certain historical influence as it appears that Signor Mussolini has attributed his abandonment of socialism to the teaching of the author. G. T.

Turbulenz. Physikalische Statistik und Hydrodynamik, by Dr Hans Gebelein, V.D.I. 177 pp. (Berlin: Julius Springer, 1935.) RM. 12.50; gebunden RM. 14.

The object of this book is to give a systematic account of the application of statistical methods to the problems of turbulent motion in liquids. The subject is one of immense importance and constitutes the great outstanding problem of physical hydrodynamics as distinct from mathematical hydrodynamics, the main object of which appears to be the construction of elegant and soluble examination questions.

In physical hydrodynamics, in which the object is to investigate the actual properties of real fluids, almost all the difficulties arise from the development of turbulent motion. On the Continent an immense amount of research has been done by Prandtl, von Karman, and by Burgers; while in England we are indebted to G. I. Taylor for a magnificent series of investigations which have recently culminated in the publication of four papers in the issue of the *Proceedings of the Royal Society*, September 2, 1935. Unfortunately the author of this monograph ignores almost entirely the work of G. I. Taylor (whose second initial is given as J.) and the work of Burgers, the only account of which in English is to be found in the first volume of the *Reports on Progress in Physics*, published by the Physical Society. Within these narrow and self-imposed limits, Dr Gebelein gives an admirable account of statistical methods in general and of their application to the extremely

difficult and complex problem of turbulent motion. The inclusion in a single monograph of the wide researches of Prandtl and his co-workers is an extremely valuable and important piece of work, and all those who are interested in these hydrodynamical problems will find this book indispensable. G.T.

Low Temperature Physics, by L. C. JACKSON. *High Voltage Physics*, by L. JACOB. Pp. vii + 134. (Methuen's Monographs on Physical Subjects. London: Methuen and Co., 1935.) Each 3*s*.

This is an age of monographs, for the advances in various branches of physics are so uneven that a comprehensive treatise on physics is often out-of-date in parts before it reaches the public. These small volumes should prove of material assistance to the student reading for an honours degree and also to the research worker in other branches of physics. In about one hundred pages the field defined by the title of each book is surveyed in a clear and orderly manner.

In the volume on low temperature the subject-matter is restricted to temperatures not higher than that of liquid air, and most of it is concerned with the region below 20° K. which is accessible only in specially equipped cryogenic laboratories. We are witnessing in this country at the present day a revived interest in low-temperature research and there is a prospect that this country will regain the supremacy it had a quarter of a century ago, when the Royal Institution was the centre for cryogenic work.

The volume on high-voltage physics is concerned with the effects on matter of voltages of from about 1 kV. to 1000 kV. and more. The opening chapter of the book contains an admirable survey of methods for the production and measurement of high voltage. Most of the results so far obtained on dielectrics are to some extent empirical owing to the complex structure and behaviour of the materials examined. So much investigation work will be necessary before the subject is placed on a theoretical basis. Admirable as these volumes are for the object in view, yet one wishes they could be supplied to the student at a lower price than 3*s*. per volume. E. G.

Electric Welding Practice, by A. G. ROBIETTE, B.Sc. 324 pp., 87 illustrations, including 3 folding plates. (Charles Griffin and Co., Ltd., 1935.)

With the rapid development in electric-furnace technique that has taken place in recent years, the need has arisen for a new text-book on the subject. The author of the book under review outlines metallurgical practice as carried out in electric melting-furnaces, and discusses the requirements of metallurgical processes in relation to the type of electric furnace which has been found most suitable. The book illustrates the enormous developments that are occurring in the application of electricity to the melting and refining of metals. The subject is one which presents many interesting problems to the physicist in connexion with the design of high-frequency furnaces.

In writing the book, the author has drawn on his experience as metallurgist successively to the Electric Furnace Company, Ltd., and the Birmingham Electric Furnaces, Ltd.

R.G.

ERRATUM

"The dependence of sensitivity of the selenium-sulphur rectifier photoelectric cell on the obliquity of the incident light, and a method of compensation therefor," by GEO. P. BARNARD, *Proc. phys. Soc.* **48**, 163 (1936).

In figure 9 illustrating the author's reply to the discussion,

for "Soil" *read* "501 L"

Phot. Kodak Ltd.

THE RT. HON. LORD RAYLEIGH, M.A., Sc.D., D.Sc., LL.D., F.Inst.P., F.R.S.

President of the Physical Society, 1934 to 1936

Frontispiece

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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SOME REMINISCENCES OF SCIENTIFIC WORKERS OF THE PAST GENERATION, AND THEIR SURROUNDINGS

BY LORD RAYLEIGH, SC.D., D.SC., LL.D., F.R.S.

Presidential address, delivered January 24, 1936

§ 1. INTRODUCTION

THE composition of a presidential address is a matter of increasing difficulty. The supply of material for general comments on the methods and point of view of physical science hardly keeps pace with the demand. And as to the subject-matter of the science, the writers of books small and large are so active that as soon as a subject becomes ripe for general discussion the field is pretty sure to have been occupied already.

Partly under a sense of these difficulties and partly under the urge of some of my official colleagues, I shall depart from precedent, and take the opportunity of telling you something of my recollections of eminent scientific men of a past generation, and the circumstances under which they worked.

There is a difference of opinion as to how far personal idiosyncrasies and details of private life are worthy of record when they have little direct bearing on results. Usually such details of the lives of scientific workers are but scantily preserved, and to judge by the frequency with which the few available details are quoted and re-quoted, one may guess that most people are eager for them, and wish that contemporaries had handed them down to a greater extent than they have done.

For my part, I think that the history of science is quite as much involved with the personalities of the men who have made it as is any other kind of history. The familiar process of digesting original memoirs into text-books, however necessary, can only be accomplished at the expense of some sacrifice of true historical perspective; and the limitation of knowledge and the narrowness of the basis on which generalization rests are too often lost sight of in the process. To know something of the personalities of the men of science themselves, the conditions of their lives, and the point of view from which they worked, may often be a useful corrective to this tendency. Those who have had the good fortune to be in personal contact with the great workers of the generation above them should not neglect to record what they think may possibly be valued by posterity. There is no doubt that this duty has

been too little regarded in the past. It is hard to realize when one is young that what we see to-day may be gone to-morrow and irretrievably forgotten the day after: and still harder to realize how eager posterity may be to know it.

§ 2. LORD KELVIN, O.M., 1824–1907

Lord Kelvin was an intimate friend of my Father's, and I have told something of their relations in my book *Life of Lord Rayleigh* (Arnold, 1924). However, as I had the privilege of knowing him intimately from almost my earliest recollection up to his death in 1907, some further reminiscences can be gleaned which did not find a place in that book.

Lord Kelvin's mental activity and vigour were at all times most remarkable. He never seemed to be tired, or disinclined to discuss any scientific subject that might come up, and was always ready to do calculations in any spare moment. These were done in a quarto note book, his famous "green book" which he carried for the purpose. He wore tail coats with large side pockets, rather like a gamekeeper's pockets, in one of which the book was kept. His work was done in a large and rather unformed, but perfectly unambiguous handwriting. If there was anything Lord Kelvin avoided, it was cloudiness of expression: and the legibility of his handwriting was, in my mind at least, associated with this trait. The "green book" was produced, and the calculations proceeded with, on what might seem most unsuitable occasions. He seemed to find distractions rather helpful than otherwise, and would bring his work for preference into the drawing-room where ladies were gossiping, rather than avail himself of a quiet room. He would join in their conversation at intervals. In the laboratory, while waiting for something to be got ready to show him, the green book was produced, and I have on occasion been pressed into service to look out logarithms for him, and read them out, while he entered them. To be as insensitive to interruption as Lord Kelvin is a very valuable gift, and an unusual one. He did not always realise that other people lacked it. I have heard that there was a saying in the natural philosophy department at Glasgow that "the Knight [Sir William Thomson] cometh, when no man can work". The work of calculation went forward during train journeys, or in a hansom cab. During the sittings of the Royal Commission on Arsenical Poisoning from Beer (1901), of which he was chairman, he would put his own questions to a witness, and then relapse into calculations while his colleagues were putting theirs: and I have even seen him similarly occupied when sitting on the platform during a not very inspiring presidential address to the British Association. Fountain pens were not then much in use, and I think everything in the book was written in pencil. The photograph, fig. 1, shows Lord Kelvin, probably in about his sixtieth year, with his book. Note the side pocket in which it was kept. Lord Kelvin was always carefully dressed, in well-cut and reasonably new clothes appropriate to the occasion, with immaculate linen. He told us that when he was an undergraduate at Cambridge no member of the University would have thought it consonant with his position in life to wear any other garb than frock coat and tall hat or academical dress when walking in the main streets of the town.

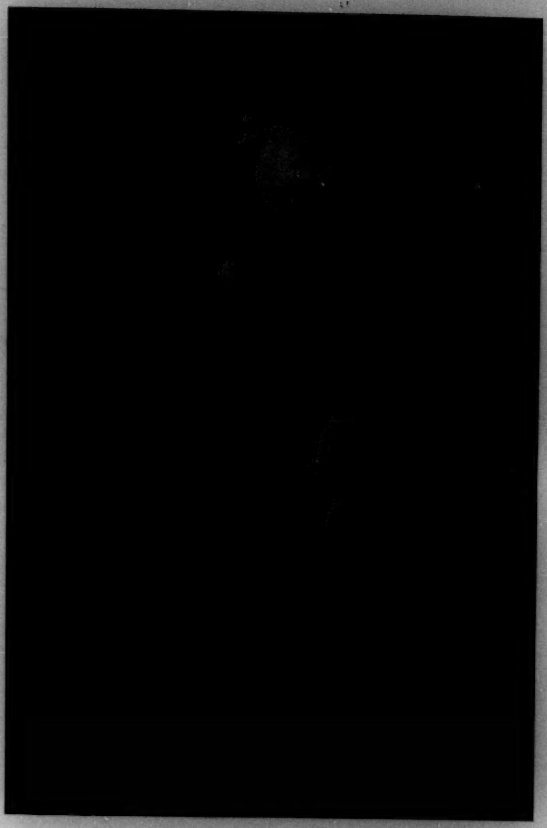

Figure 1. Lord Kelvin with his green book.

Facing p. 218

In the earlier days of his Glasgow Professorship, Lord Kelvin was a pioneer in encouraging students to work in his laboratory: but it cannot be said that he had anything amounting to what would now be called a school of experimental physics. Lord Rayleigh, for instance, about the year 1866, was anxious to get some initiation into the practice of experimenting, and found it very difficult to do so. Cambridge afforded practically no help, and he had never even heard of Glasgow as a possible alternative. Lord Kelvin's idea as to occupation for elementary students was not altogether the modern one. He thought that they should make themselves useful, chiefly in connection with the development of his commercial inventions. Sir William Ramsay used to say that he was set to work to take the kinks out of old copper wire! However, he eventually succeeded in getting hold of one of Lord Kelvin's electrometers, and made some measurements with it on electromotive forces.

One subject which Lord Kelvin was interested in discussing was the obscure phenomenon of globe lightning. He took up the point of view that such an effect could not be explained by or reconciled with the known laws of electrical conduction in closed circuits and that the accuracy of the recorded observations upon it must be denied. Sir George Darwin told me that on one occasion Kelvin had felt compelled to yield to some particularly detailed evidence on this matter from a competent witness, and for the moment frankly abandoned his old position. But, next time the subject came up, I do not know after what interval, Darwin was interested to observe that Kelvin had relapsed into his incredulous attitude. I think this psychological history is not an uncommon one. Belief in the marvellous involves a painful effort to a cautious and careful thinker, and unless the belief is constantly refreshed and maintained by a supply of new evidence, a relapse is very apt to follow. As to the truth of the phenomenon itself, reference may be made to a paper by Jensen[1] in which photographs are reproduced. The luminous objects shown on them are large, and by no means spherical.

Lord Kelvin's engineering methods were interesting and characteristic. He had probably never had practical familiarity with the use of tools; indeed it is not easy to visualize him as successfully driving home a screw: though one who, like myself, only knew him as an old man can hardly judge, and it is to be remarked that in his youth he was a successful oarsman, and played well on a wind instrument, both of which involve the appropriate kind of personal dexterity. His insight into the essentials of an engineering problem was, needless to say, very great, and his descriptions of his inventions such as his compass and his sounding machine are models of what such descriptions should be. They were composed with great care, and I have heard that in writing them, and in composition generally, he would sometimes pause for long periods before he could find the right word, or shape a sentence in the way that would satisfy him.

In designing his instruments and other mechanical constructions, he did not make use of machine drawing. His method was to get something actually made and then criticize it, and have it modified accordingly. This plan had its inconveniences. When long afterwards it was desired to copy Lord Kelvin's tide predicting machine, it was found that no drawings of the rather elaborate mechanism

had ever existed; and I believe that it had to be drawn out *de novo* from the existing machine. I believe, too, that his electrical instruments were made in the same way, being built up on a mahogany board from his verbal directions.

The view was sometimes taken, notably by Tait, that it was a prostitution of Kelvin's great abilities to devote himself to engineering and invention. It is doubtful, however, whether this view is really tenable. His brother, Professor James Thomson, cared mainly for engineering* and we may well suppose that Kelvin too had a strong natural bent in that direction. This is not inconsistent with his keen appreciation of the financial benefit of his inventions.

There was a certain competition for Kelvin's time and attention between Tait and Fleeming Jenkin. Kelvin came to stay with one or the other of them when he was in Edinburgh. With Tait he was writing the *Treatise on Natural Philosophy*. [Opinions differ as to who did the lion's share of this. Sir Alfred Ewing, from whose conversation (May 16th, 1932) I gained some of these details, thought that it was Tait. Lord Rayleigh, however, had the opposite impression.] Jenkin collaborated in Kelvin's inventions in connection with submarine telegraphy. He conducted all commercial correspondence connected with the very profitable royalties, and did this well, successfully avoiding litigation. Kelvin's compass inventions, on the other hand, involved him in a good many lawsuits.

Lord Kelvin's mind was not readily satisfied with any theory which did not lend itself to the formation of a mental picture. He required mechanical analogies, and it was perhaps partly for this reason that he was so much dissatisfied with the electromagnetic theory of light, which (in some moods at least) he did not consider could rank as a theory of light at all. His point of view was difficult to grasp: but one day when he was talking in this general sense, I ventured to remark that it seemed to me that at any rate it was a great step to have shown that the velocity of light could come out of electrical measurement. Lord Kelvin did not seem to admit that this remark was at all to the point when Maxwell's theory was under discussion. I asked whether it was not true that Maxwell had been the first to point out this relation and had he not done it in connexion with his theory? Lord Kelvin said no, it had first been pointed out by Kirchhoff, who was discussing conduction along wires. Needless to say that he was quite right, though I have only identified the passage with the help of Sir Joseph Larmor, while writing this address.†

The following anecdote, which I have from Professor George Forbes, who was an eye-witness, further illustrates his antipathy to this general line of thought. The

* There was some personal resemblance between the brothers, and devoted affection. On the other hand, James Thomson was slow and cautious, in contrast with his brother's eagerness and enthusiasm, and would keep his scientific work unpublished for years. Lord Kelvin was often impatient with this.

† See G. Kirchhoff, "Über die Bewegung der Electricität in Drähten," *Ann. Phys.*, Lpz., **100**, 210 (1857), or *Gesammelte Abhandlungen*, p. 147. Maxwell's first mention of the relation appears to be in the B.A. Reports, 1863, and he does not mention Kirchhoff in this connexion either then or later. It is strange that so little should be known of this matter. It is not mentioned, so far as I know, in any British text book on electricity, and the few veterans who survive from the Maxwellian era seem for the most part to be unaware of it. There is a full account in G. Wiedemann's treatise, *Die Lehre von der Electricität*, **4**, 1076 (1881), but it is strange that when he comes to deal with Maxwell's results on p. 1178 he makes no further reference to Kirchhoff. A reader who consulted the latter passage alone would almost certainly conclude that Wiedemann knew nothing of Kirchhoff's work.

scene was at the British Association meeting at York in 1881, when Lord Kelvin was president of Section A, Silvanus Thompson wrote up some equations on the blackboard dealing with Maxwellian electro-magnetics[2,3], which did not commend themselves to Lord Kelvin. For some reason, possibly with the idea that the president of the section should not speak controversially, he did not voice his objections, but as soon as S. P. T. had finished speaking, Lord Kelvin limped up to the blackboard and rubbed the equations out with a duster. S. P. T. took this in good part, and when Forbes reminded him of it some time later, he said that he had not given it a second thought. As is well known, it is to him that we are indebted for a masterly biography of Lord Kelvin.

Lord Kelvin had humour of a kind, but it was somewhat elementary, and he did not disdain puns, which, I suppose, were still fashionable when he was young. When he spoke of Hittorf's investigation on cathode rays, he said that he had "hit it off" very well. On this subject he was always very emphatic on the merits of Varley's short paper in the Royal Society's *Proceedings* in 1871[4]. Varley had shown that a light suspended vane was strongly repelled when placed in the path of the rays, anticipating Crookes' experiments on this matter. However, the forces brought into play in such experiments are much too large to be attributed to the direct effect of the bombardment, and this was pointed out in a paper by Starke[5], which I showed to Lord Kelvin. When I asked him next day what he thought of it he said he had not had time to read Starke's paper, but that he did not think it at all "strong"!

Rather more subtle was his remark to an electrical Journal, to the effect that one of his correspondents had better be submitted to the action of the "Silent Discharge".

Lord Rutherford reminds me of the following incident, of which I am not altogether proud, but which ought to be recorded as showing Lord Kelvin's complete freedom from self-consciousness and his love of truth. It was in May 1904, when he and other scientific friends, Rutherford among them, were paying a visit to my parents. Lord Kelvin was enthusiastic in his interest in radioactivity, but much averse to Rutherford's views which regarded the energy as derived from atomic sources. Lord Kelvin considered at that time that the energy was drawn from the surroundings in defiance of the second law of thermodynamics, and he would sometimes say when discussing the matter with laymen, that he had hoped to go down to posterity as having formulated this law, and now he was compelled to admit that it was mistaken! He was arguing emphatically with Rutherford and myself against the atomic origin of the energy; so far as I remember he maintained that it was self-contradictory to appeal to atomic disintegration, the very definition of an atom, and the derivation of the word, implying that it did not disintegrate. I was enthusiastic for Rutherford's view, and with some lack of proper respect and deference, I asked Lord Kelvin if he would make a bet of five shillings with me that within three (or it may have been six) months he would admit that Rutherford was right. He seemed to be delighted with the proposal, and told the ladies about it, saying that he felt pleased that such confidence was placed in his good faith: for (he said) it was only by his own voluntary admission that he could possibly lose his money.

Within the allotted period Lord Kelvin's views had come round, and at the meeting of the British Association in the autumn of that year he made a public pronouncement in favour of the internal origin of the energy of radium[6]. I certainly never expected to hear any more about the bet: but next time I saw him, he came up to me at once and said: "I think I owe you five shillings. Here it is!"

But this was not the end of my troubles. I had become interested in the problem of the earth's heat, which, as Rutherford had suggested, might perhaps be explained by the radio-active matter contained in it. I made a series of determinations of the amount of radium in typical rocks, by getting them into solution, and boiling out the radon generated on standing. The result showed that there was enough radium even in the outer parts of the earth to account for the observed outflow of heat. I published a paper on the subject, but it soon got me into disgrace with Lord Kelvin. I received the following letter from him:

15, EATON PLACE, S.W.
June 11th, 1906.

Dear Robin,

I have been reading your last R.S. paper with extreme interest. Your experimental determinations of radium in rocks and meteorites are (it need not be said) exceedingly valuable and important.

But in your speculations on the "Earth's Internal Heat" you have apparently forgotten what you told me two years ago when you were showing to the R.S. what I called your perpetual motion;* that the energy of radium is all spent (? or half spent) in 1500 years. You have in your present paper reckoned on a *uniform* rate of expenditure of heat by radium in granite; the same rate as that of radium per gramme in bromide of radium. Surely on your own principles all the radium-energy of any mass of granite, large or small, and of any stony meteorite, would be all spent in the course of a few thousand years; and no granite or other mineral could now possess the unexhausted radium which you find in it. The fact that you do find it proves that radium in that combination *does not* generate heat at all, or generates it only at rates vastly less than the rate proved by experiment for separated radium bromide.

Yours,
KELVIN

I have not kept any copy of my reply but it may be reconstructed in outline from Lord Kelvin's next letter, which is given below:

15, EATON PLACE, S.W.
June 14th, 1906.

Dear Robin,

What you say in your letter of Tuesday does not give reason to believe that granite has been giving out heat for millions of years. I knew Soddy's work on production of radium from uranium, and I saw the beginning of his last experiment which is now being continued.

There is good reason I believe for regarding underground heat, and sun-heat as originally due to expenditure of gravitational energy in the coalition of the matter constituting earth and sun.

* This is the experiment which has become known as the "radium clock".

I am glad you are coming to London tomorrow. Will you and your wife come to tea or lunch some day soon? or will you come to breakfast 9.15 or 9.30 on Saturday. This would give us opportunity for a good talk over energy of gravity, and of radio-activity which I think is probably due to gravity.

Yours,

KELVIN

I accepted the invitation to breakfast, and afterwards we adjourned into his study, when he introduced me to his mathematical secretary, Mr George Green. "Not the George Green you know of", he said. His papers were neatly filed in rows of appropriate boxes—I remember one labelled "Income Tax". We soon got down to business. My paper was produced, and Lord Kelvin pointing to the conclusion, said emphatically that he did not believe for a moment that it could be true. I struggled for nearly two hours to get him to tell me exactly at what point he dissented, but without, as it seemed to me, any progress. After that, it was necessary for some reason to discontinue the sitting, but Lord Kelvin seemed anxious to resume it at the first opportunity. I was flattered, but a little puzzled by this, since he had not seemed to attach weight to anything I had to say.

I next saw him when he called unexpectedly a little later at my house at Cambridge. It was in the morning, and he was directed to the laboratory on the far side of the garden where I was at work. I heard my christian name called, and looking out to see who it was, there was Lord Kelvin, his white beard streaming in the wind. I went down and brought him up. His thoughts still seemed to be running on my heretical paper, and he was anxious to see my "rock broth", by which he meant the solutions of rocks used for the determination of radium by means of radon. He seemed disappointed when I had to tell him that it had been thrown away when the determinations were finished. However, I showed him whatever I was doing at the time, and as usual he was very interested and enthusiastic, as indeed he always was over experimental work. He took his leave, and I think that that was the last time I saw him. He died a few months afterwards.

However violently Lord Kelvin disagreed with people on scientific matters (and it was obvious that he did not mean half of what he said—if he had done so their views would not have been considered worth his powder and shot) he was always most careful not to say or write anything that would needlessly hurt their feelings. He was essentially courteous, and rightly expected to receive courtesy in return. On the occasion of the Jubilee of Sir George Stokes' Professorship at Cambridge, he got up among a surging crowd of people at an evening reception at the Fitzwilliam Museum and gave an *extempore* address on Stokes' scientific career. What he said was probably over the heads of the audience, even if they had been well able to hear it, which they were not. As might be expected under the circumstances they soon began talking, and Lord Kelvin did not conceal his anger.

Indeed he was not very apt at adjusting what he said to the capacity of his audience. He said the thing because it interested him, rather than because it was particularly likely to get "across the footlights". Very often this did not matter. His own interest in what he was saying was infectious, and kept his audience

pleased. Young ladies whom he met in society would be delighted to receive his confidence in this way. On the other hand, I remember Mr Joseph Chamberlain remarking that when scientific men were good enough to explain to him something of their problems and conclusions he could usually understand, but that Lord Kelvin left him completely mystified.

Lord Kelvin was a violent anti-Home Ruler, and it was probably this that brought him into contact with Chamberlain. It is curious to read[7] that his father, Professor James Thomson, had in childhood been a witness of the severities used in suppressing the Irish rebellion of 1798, and was led to sympathise with the rebels. It would be interesting if we knew fully the development of Lord Kelvin's views on this subject.

In his prime, Lord Kelvin cannot have been wanting in boldness of conception and faith in the possibility of success in heroic enterprises. His work in connection with the Atlantic cable is evidence of this. In old age he became more sceptical. He was curiously positive in his hostility to the conception of an aeroplane as a practical thing and he did not live quite long enough to see his views falsified. Motor cars he did see, but he did not like them, and was very emphatic in maintaining the wisdom and necessity of the early law which limited the speed to ten miles an hour.

I owe the following to Sir Hugh Shaw-Stewart. Mr Speaker Peel came on a visit to Ardgowan, at the mouth of the river Clyde. He had arrived by the night train from London, and had some little time on his hands before breakfast and before his host and fellow-guests had put in an appearance. He wandered out into the garden, and climbed to the ramparts of the old border tower, which was the original home of the Shaw-Stewart family, and which looks out over the sea towards the south. There he encountered a friendly old gentleman, not known to him, who was earlier than the other guests, and they fell into conversation. The old gentleman looked out to the south over the sea with a faraway dreamy look in his eyes and said, "It is strange to think that there is nothing between us and Spain!"

Mr Speaker Peel in fact thought it so strange that he was inclined to form an unfavourable opinion of the old gentleman's mental condition. They went in to breakfast, and the unknown was introduced as Sir William Thomson. Thereupon, Mr Speaker Peel thought that his first impressions might need to be reconsidered. He took an early opportunity of consulting the map, and soon found that the paradox was confirmed.

Lord Kelvin in his later years was somewhat deaf, and his desire for accuracy and precision made him unwilling to try to guess or reconstruct what had been said from imperfect indications, as most people are willing to do. This made conversation with him across the table rather exacting. He was fond of going to the theatre with Lady Kelvin, but when he did not hear, he asked her to repeat, and this happened so often that the occupants of the neighbouring seats were visibly annoyed. Lady Kelvin was ultimately forced to discourage theatre-going for this reason.

This brings me to say a word about the relations between them, which, at all events, so far as friends could judge, were ideal. They were entirely dependent on

one another. It was pretty obvious that Lady Kelvin did not know or care much more about science in the abstract than ladies in general do, but Lord Kelvin did not seem to be at all damped by this, and would unburden his mind to her at length about the most abstruse matters, while she placidly went on with her knitting. Professor Zeeman tells me that Lord Kelvin went into transports of delight when he showed him "the magnetic splitting of the spectrum lines", and was eager that Lady Kelvin should see it too. Lady Kelvin however did not make much pretence of sharing his enthusiasm.

It may be permissible to mention in passing a matter personal to myself. When I was engaged to be married in 1904, Lord Kelvin insisted on going with Lady Kelvin to select a wedding present; a pair of old silver cups were chosen, and they are among my treasured possessions. I have brought them to show you.

Lord Kelvin's last illness was aggravated, it was thought, by anxiety about Lady Kelvin's health, which was far from satisfactory. However, she made a good recovery, and survived him for a few years. But the light had gone out of her life, and she could not face the effort of going alone to houses where she had been accustomed to go with him.

These reminiscences have necessarily dealt in the main with Lord Kelvin as an old man, for it is only so that I knew him. Many of them, I am afraid, reveal some weaknesses that are incidental to that period of life, and those who knew him in his magnificent prime would have been able to draw a portrait worthier of the subject. Nevertheless there was much to admire in his old age, particularly from the human point of view. He was as enthusiastic as a boy, and entirely unspoilt by his success in life, and indeed apparently unconscious of it. To over-emphasize his own achievements or to dwell on them at all except in so far as they were interesting and relevant in themselves was a thing quite foreign to his point of view. The impression he generally produced on strangers was that of a dear old gentleman, and further acquaintance did not tend to change it. But with all his simple kindliness, his presence was on occasion most dignified and impressive, and the same may be said of Lady Kelvin, his devoted wife.

§ 3. ROYAL INSTITUTION

The old laboratories of the Royal Institution as they were towards the end of the last century, during the period of Dewar's large-scale liquefaction of the permanent gases, and Rayleigh's work on the isolation of argon, are but a memory. The rooms have for the most part been altered past recognition in the rebuilding operations and the men who worked there when I first knew the place have all passed away. It is worth while to try to reconstruct the scene in a verbal portrait; and I am encouraged to make the attempt by the circumstance that valuable contemporary photographs exist which were taken by Miss Reynolds and bequeathed to the Institution. Many of these have never been published, and I am allowed to reproduce a selection from them here. It is impossible altogether to avoid ground already covered in my *Life of Lord Rayleigh*, but I shall have much to say that is not to be found there.

In those days there was no "Director" of the Institution. Sir James Dewar,* who held the Fullerian Professorship of Chemistry, lived in the historic rooms on the top floor, which had been occupied by Faraday and Tyndall, and was "Superintendent of the House", exercising a general supervision over the building and staff. His rule was not supposed to extend to the physical laboratory, which was the domain of the Professor of Natural Philosophy (Lord Rayleigh).

Rayleigh had accepted the appointment in 1887 on the understanding that he would continue as before to work for the greater part of the year in his own laboratory at Terling, and that he would only be at the Institution during the season before Easter. Further, that the Institution would pay part of the salary of his assistant, George Gordon, who came up with him. During the season before Easter he gave a course of six afternoon lectures and a Friday evening discourse.

The physical laboratory, as it was left by his predecessor Tyndall, consisted of three rooms above the level of the street, but below the lecture room. They were situated immediately over the chemical laboratory in the basement, and the vibration from the machinery installed there by Dewar made many kinds of physical measurement impossible to carry out.† However, Rayleigh's season there was limited, and a good deal of his time was occupied in preparing for the afternoon lecture on Saturdays, and devising demonstration experiments, so that not very much systematic research work was attempted.

When Rayleigh came there he found the equipment very inadequate, and reported so to the Managers. There was no strict allocation of the available apparatus and supplies of material between the two laboratories, and, as may be imagined, considerable forbearance was needed to make such a system tolerable. I was about to say mutual forbearance, but the term hardly seems applicable, as the forbearance was nearly all on one side. Rayleigh and his assistant Gordon found an almost complete want of ordinary stores such as screws, copper wire and the like. They did their best to remedy the deficiency: but with little advantage, for their store was at once regarded as a plundering ground by the Scottish marauders from downstairs. Not being there continuously, they were not in a strong position for guarding these treasures and any attempt to lock them up was resisted as "contrary to the custom of the Institution". I believe Gordon was ultimately reduced to hiding these elementary necessaries.

Rayleigh was assigned a grant by the Managers to supply the most serious deficiencies of apparatus but here again he was met by the same difficulty. For instance, he felt the want of an electric motor for general purposes. He took steps to provide one and enjoyed the use of it for a time. But when he returned the next year he found, somewhat to his annoyance, that it had been permanently absorbed for driving a lathe downstairs.

As I have already explained, Rayleigh did not usually attempt anything very important at the Royal Institution laboratory apart from preparing his lecture

* Knighted in 1904.

† It has been thought probable that this vibration set up the mischief which ultimately resulted in the collapse of the library ceiling.

Figure 2. The Physical Laboratory, Royal Institution. Apparatus for concentrating argon.

Figure 3. The same. Small-scale argon apparatus.

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demonstrations. The chief exception to this was in the large-scale separation of argon from air. I say large-scale only relatively to the standards of that time, when 50 cubic centimetres was considered valuable. He had separated a quantity of that order of magnitude in his private laboratory at Terling by the process of sparking air with excess of oxygen, over caustic alkali, and the next step was to make a much larger supply, for the determination of its physical properties, more especially the density. His annual before-Easter season in London lent itself very well to dealing with this matter, since the alternating electric supply was available there, while at Terling it was necessary to run a gas engine continuously and even so the power was not enough.

About 3 litres of argon were required to fill the globe in use at Terling for weighing gases. This involved the absorption of 300 litres of nitrogen, or about 800 litres of the oxygen-nitrogen mixture. The vessel used was one of 20 litres capacity cooled by a water-jacket above, as may be seen on the right of the photograph (fig. 2). The Swinburne "hedgehog" transformers (open magnetic circuit) are seen to the left of it and then the aspirator bottles used for measuring the rate of absorption. The gas holder containing the main supply of mixture is at the extreme left.

The low-frequency note of the transformers was heard from morning till night during this period: and any occasional intermission left a sense of something wanting. Dewar, passing on the staircase and, as usual, humming a tune to himself, was struck by this, and came in remarking: "I don't hear your hum." "No," thought Gordon to himself, "but I hear yours."

The manipulation of the apparatus was not free from danger, and as a precaution Rayleigh made it a rule for himself and others to stand on an insulating mat and to *touch only one thing*. The rubber door mat was noticed by Mr Swinburne* when he came in to advise about the transformer, and he remarked that the "rubber" mat probably contained about 1 per cent (?) of indiarubber. (At that time the price of raw rubber was very high, and the quality of "rubber" goods, e.g. the rubber tubing used in laboratories, was deplorable.)

The operation went on for three weeks. It was debated whether it should be left going at night, but there was no one but one of the porters to attend to it, and "Richard"†, who apparently had no confidence in the man, said in his laconic way, "better not". Rayleigh, who was hesitating, was impressed by this, and contented himself with working during the hours when the scientific staff were there. The concentrate, not yet free from nitrogen, was removed to Terling for the final purification and weighing.

There is a still larger sparking globe of 50 litres capacity preserved at the Royal Institution as a relic. It is fitted with massive platinum electrodes, and was cooled internally with a fountain of alkali, instead of being water jacketted. This vessel was used in later experiments to develop the method, but its historic interest is less.‡

Fig. 3 shows another view of the physical laboratory. The most conspicuous

* Now Sir James Swinburne, Bart., F.R.S.

† See below, p. 236.

‡ The sparking vessel used at Terling, similar to that of figure 2 but smaller, is now at the Science Museum, along with the weighing globes and other relics of Lord Rayleigh's work.

object is the small sparking vessel of test tube form, standing over alkali, and the voltmeter used to feed in oxygen, or hydrogen for the removal of surplus oxygen. This was used for analyzing small samples of gas for their argon content.

The chemical laboratory of the Royal Institution was in the basement, below the level of the street. When I first saw it, probably about 1889, the most conspicuous object in it was a tube 18 metres long, which was filled with compressed oxygen for observations on the absorption spectrum. As his work on the liquefaction of gases progressed, and as the scale of operations increased, it gradually took on more and more the aspect of a factory, full of machinery run by means of shafting from a large gas engine.

The earlier method of liquefying air depended on compressing it at the temperature of liquid ethylene evaporating under the air pump. The ethylene was not commercially available, and used to be made in a glass carboy from alcohol and sulphuric acid. It was stored in a gas holder in the small well or yard outside the big window of the laboratory. This may be seen in fig. 4.

By this method Dewar liquefied air on a scale never before attained, and showed the properties of the liquid for the first time to large audiences.

Later about 1895 the Linde method of liquefying air by means of the Joule-Thomson effect came into use. It was not easy to realize that precooling by more easily liquefied gases could be dispensed with, and Dewar never gave up the idea of "cascade". He eventually discontinued the use of ethylene, but carbon dioxide was always retained. A large machine was ultimately built, capable of producing 20 litres of liquid air per hour, and this was preparatory to the liquefaction of hydrogen—the culminating triumph of Dewar's life. As is well known, this was done by passing the compressed gas, precooled to the temperature of liquid air boiling *in vacuo*, through a coil, and allowing it to expand through a valve at the bottom, with regenerative cooling. This was in 1898–9.

It was soon found that the great trouble in liquefying hydrogen was the blocking of the tubes by solidified air, or other impurity in the hydrogen. The hydrogen commercially obtainable in cylinders at that time was not good enough, and it was necessary to prepare it from zinc and sulphuric acid. The generator was in the yard outside and the hydrogen was stored under pressure in a row of tall steel cylinders each capable of holding 300 cubic feet. The gas was admitted at the bottom and drawn out for use at the top. It was necessary to go up a 12 ft. steel ladder to get to the exit valves. The cylinders, I was told, were made from disused big guns from Elswick.

When all this machinery had been installed, little ordinary laboratory accommodation was left, except the bench under the large sloping window, where a row of vacuum vessels may be seen hung up (fig. 4). Later, a room was added forming part of the house next door, which had been bought by Dr Ludwig Mond for the Davy-Faraday Laboratory. Dewar is shown in this room in the well-known photograph prefixed to his collected scientific papers and also to the Royal Society obituary.* It is now used as the workshop. Dewar must, I suppose, have really

* See reference (8) In selecting the photographs here reproduced, I have excluded any which can be found elsewhere.

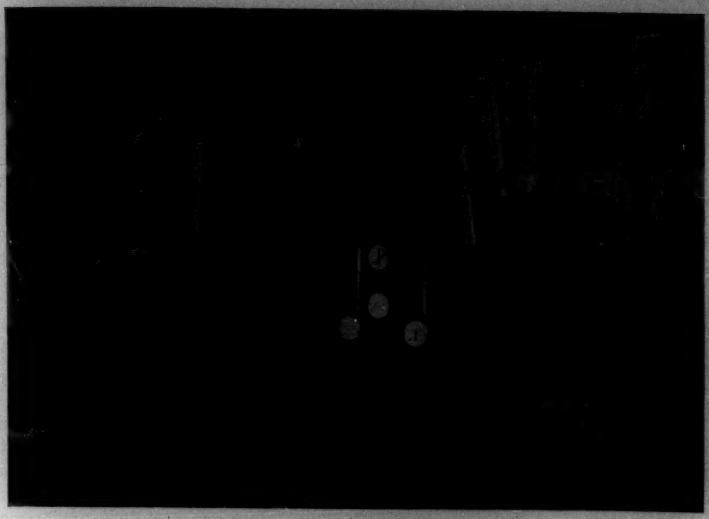

Figure 4. The Royal Institution. Chemical Laboratory. Plant for liquefying gases.

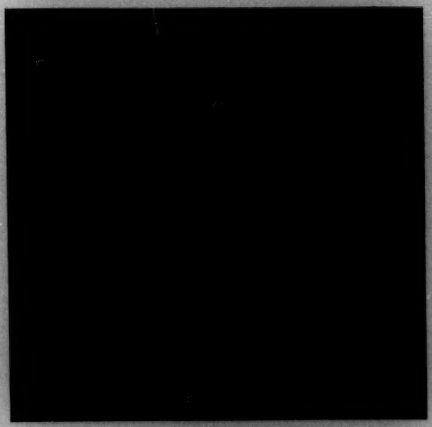

Figure 5. R. N. Lennox in the Lecture Theatre.

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been grateful to Mond for his magnificent gift to the Institution, but his tone scarcely suggested it, and in talking to Rayleigh he took up a singular attitude, apparently regarding this generous benefactor as a sort of suspect who was on his probation.

Having liquefied hydrogen on a large scale, Dewar proceeded to an attack on helium. Some account of his ideas on this matter will be found in his presidential address to the British Association at Belfast in 1902, when he described the procedure which ultimately succeeded in the hands of Kamerlingh Onnes, namely regenerative expansion with precooling by liquid hydrogen boiling in vacuum. I saw Dewar's apparatus in course of construction. The regenerative coil was contained in a vacuum glass. Outside this was a larger vacuum glass (see below, p. 234) to contain liquid hydrogen and outside this again a simple glass cylinder to contain liquid air. Two outer glass vessels were to afford thermal insulation. The liquid helium, had it appeared, could only have been examined through no less than seven separate glass walls, or fourteen surfaces.

The observation that helium was contained in the gas from the Bath Spring was made by Lord Rayleigh, who had known the town of Bath well from his youth up, and was aware that gas bubbled up from the hot spring. This gas had been classed as mainly nitrogen, and he had originally thought that it might really consist in the main of argon. This did not prove to be the case, but it did contain some argon and helium. Dewar, anxious to obtain helium for his attempts to liquefy that gas, decided on using the Bath Spring as a source. He got the consent of the Corporation of Bath and went to considerable expense to arrange for collecting the gas on a large scale, installing near the spring a gas holder for collecting it, and a compressor to put it into steel cylinders for transport to London. There it was treated for extraction of helium. The helium present was only one-thousandth part of the whole, and was necessarily expensive when produced in this way, by transporting the crude gas from a distance. However, any method of obtaining helium at that time would have been costly: no doubt that had been faced, and was not the most serious objection. The real trouble was that the helium from Bath gas contained a considerable proportion of neon, which could not readily be removed by the methods of purification adopted. In the opinion of Mr W. J. Green, who was associated with the later stages of this work, the blocking of the tubes and valves with solid neon was the principal obstacle which prevented the success of Dewar's attempts to liquefy helium, though at the time this blocking was attributed to ordinary impurities, which it was supposed had escaped removal in the preliminary processes. From this point of view, it seems a considerable misfortune for British science that helium was ever found in the gas at the Bath Spring. If Dewar had extracted his helium from monazite, as Kamerlingh Onnes did afterwards, he would probably have succeeded in the liquefaction. Nevertheless, his large-scale operations with the Bath gas may be considered the prototype of those modern ones which have led to the collection of helium in quantities adequate even for use in airships. It must have been an acute disappointment to Dewar that he was outstripped in the race to liquefy helium. But he took it with a good grace and himself gave an

exposition of Kamerlingh Onnes' work at the British Association meeting at Dublin in 1908.

This pioneer work on liquefaction of gases made large demands not only on the skill and persistence of the workers but also on their personal courage. On one occasion when I happened to be present I was struck with the iron nerve and composure of both professor and assistant. A, to me, alarming explosion rent the air of the laboratory, but Dewar did not move a muscle, or even turn to look. I asked in alarm what had happened; but it was only a good-sized vacuum flask full of liquid air which had smashed to atoms, in the hand of his assistant Lennox. The incident was not thought worthy of a word of comment except in answer to a visitor! Dewar never admitted that anything was dangerous. The most he would say was that it was a little tricky. Considering that Lennox and Heath, his two assistants, each lost an eye in the course of the work, this was certainly not an overstatement. On one occasion, at least, after a run for liquid hydrogen, a large leak developed, and the issuing hydrogen took fire, forming a sheet of flame right across the room, cutting off access to the stop valve at the top of the tall storage cylinder. Johnson, the mechanic, who was in the next room having his tea, realized what had happened, rushed in and sprinted up the ladder. The clicking of the rachet key which operated the valve at the top of the storage cylinder was a welcome sound.

I once met Sir Frederick Bramwell, who was then Secretary of the Royal Institution, in Dewar's rooms and heard him chaffing Dewar in a way that suggested that he thought his engineering practice highly unorthodox, proper factors of safety and speed limits being ignored. In the published accounts of Dewar's work on liquefaction of gases the engineering aspects are passed over very lightly, and there is a practically complete absence of dimensioned drawings such as would be really helpful to those who wished to follow in his footsteps. This contrasts with the practice of other workers in the same field, both before and since; and it contrasts also with the ample details given by Dewar himself about the vacuum vessels used for storing the liquids, and the various demonstration experiments on vapour pressures, and on solidification by evaporation *in vacuo*. The reason given was that the methods were not new and that "science derives no benefit from the description of transitional apparatus when there is no secret about the working process and how to carry it into effect". No doubt this is true up to a point, but as a matter of fact other workers were often eager to hear and see the details of Dewar's working methods, and were not allowed to do so. He disliked visitors coming unannounced into his laboratory, and on occasion would make a violent protest before he had adequately considered who the visitor was, and what right he had to be there. This more than once led to trouble and on one occasion at least Dewar apologized, saying that he had spoken hastily, but that if the visitor knew how much he had suffered from the piracy of his ideas, he would understand how it had happened.

The policy of secrecy was not altogether easy of execution. Those who came in to lecture at the Institution from outside had necessarily to have the help of the

laboratory staff in getting their lecture demonstrations arranged. The physical laboratory, whether Lord Rayleigh was working there or not, was open to them without reserve, and this made it rather difficult to carry out a different policy as regards the chemical laboratory downstairs which, from the standpoint of the members of the Institution and of the Board of Managers, was on a precisely similar footing. Indeed, I believe it is correct to say that the original rules of the Institution actually allowed the members the use of the laboratories though this rule was practically obsolete. They were, however, entitled to see what was going on, and one of them at least successfully asserted this right. Later, during the War, there was a movement among the members to insist on the laboratories being more fully utilized for war purposes and it was agreed by the Managers, apparently not much to Dewar's satisfaction, that a Committee from the Ministry of Munitions should visit the laboratory to see if they could make use of it. However, as one of them told me, they found everything covered with dust-sheets. The sheets themselves were clean, but there was a good deal of dust on the machines which they covered, and it was reasonably suspected that the sheets had been specially put on in honour of the visit. They retired discouraged, and the matter was dropped.

When, some time later, Kamerlingh Onnes was in England, he wrote asking to see Dewar's laboratory: but Dewar civilly begged to be excused showing it, saying that then no awkward questions could arise. It was difficult to see any adequate reason for all this mystery, and I think it was mainly temperamental. The usual reason for secrecy is in the commercial value of unpatented knowledge. But Dewar gave his invention of the vacuum flask freely to the world, and never made a penny by it, though he might have realized a fortune.

It is no secret, and indeed often appears in the present account that Dewar was quarrelsome. So far as I am aware those who were most conversant with the circumstances of the various quarrels generally considered him to be in the wrong. Nevertheless he was essentially kind-hearted, and if his tongue was rough, he was ready enough to respond to a friendly advance when he had cooled down, and, I suspect, attached little importance to what had passed, considering that hard words break no bones.

He was a bad sleeper, which explains and excuses much. I have heard it said that he was glad to get even three hours. He was something of an amateur pharmacologist, and had a special sleeping mixture of his own composition, which he took regularly, and sometimes recommended to his friends.

He was a generous man, and if anyone with whom he was associated needed help, he gave it unstintingly, and would not listen to a word of thanks.

His rooms on the top story, those which had formerly been occupied by Faraday, were a centre of hospitality after the Friday evening lecture. He was something of a collector of furniture. One of his treasures was a pair of bellows of Renaissance work carved with spirited figures, which he had bought (I think from Wertheimer) because, as he said, bellows were "the chemist's first implement". When these were cleaned and closely examined he found traces of a signature, with place and date,

which led him to attribute them to Benvenuto Cellini. Whether this attribution was accepted by experts I do not know.

Dewar's training had been primarily that of a chemist. His earliest investigations were on organic chemistry, but in addition he was a man of wide knowledge and essentially original scientific outlook. It was difficult to get much insight into his mental processes by talking to him, or even by listening to his lectures. He had no notion of unfolding his views in logical order, or of clearly explaining by what train of thought he had arrived at them. But however mysterious its origin there was no doubt of the value of his inspiration. The invention of vacuum-jacketted vessels naturally occurs to every one: and if they had come to be popularly called Dewar flasks instead of thermos flasks, his fame would doubtless have penetrated to a very wide public.*

The use of charcoal cooled in liquid air for producing high vacua and for isolating helium was an invaluable laboratory method, and contributed much to the success of the earlier researches on positive rays, and on the rate of generation of helium from radio-active bodies. Its value is now diminished owing to the modern invention of other methods of rapidly producing high vacua, but is still by no means negligible.

Then again, men have watched the beauties of soap bubbles from time immemorial, but it was Dewar who first penetrated the secret hidden from all other men and succeeded in making them permanent by the use of pure dust-free air. It can hardly have been anything but a happy guess that led him to this: but a guess that he alone had made and verified.

Having now said something about the leaders and their work, I wish to notice the subordinates. Rayleigh's assistant, George Gordon, who was with him alike at the Cavendish Laboratory, at Terling, and at the Royal Institution, I have already noticed in my *Life of Lord Rayleigh*. Heath, the lecture assistant, was civil and helpful, but not in any way outstanding.

Dewar's chief assistant, Robert Lennox, who was with him from 1881 to 1908, was an interesting personality, and his relations with his chief formed a curious psychological study.

My information about his life-history is fragmentary, but he must have been still quite young (not more than twenty-three) when he went to the Royal Institution. He told me that he had had a training in engineering science under Professor James Thomson at Glasgow, which had enabled him to design and make working drawings of the machinery used by Dewar in the liquefaction of gases. He was also at one time chemical assistant to W. Dittmar at the Glasgow Technical College. He does not seem to have taken a university degree, but his general scientific capacity was far beyond what is usually found in non-graduates, or for that matter, in graduates either. His services were worth more than the very limited funds of the Royal Institution could afford, and Dewar supplemented Lennox's Royal In-

* Dewar's earliest publication of the idea of a vacuum vessel dates back as far as 1874, long before his successful use of it for liquid air in 1893. There is no justification for any suggestion that he had been anticipated in the matter.

stitution salary from his own resources. Fig. 5 represents Lennox in the lecture theatre, and I am glad to be able to reproduce it as a memorial to one whose services to science have not been sufficiently recorded.*

Dewar was always careful to acknowledge the value of the help that Lennox had given him, and expressed himself as follows (1899):

"During the whole course of the low temperature work carried out at the Royal Institution, the invaluable aid of Mr Robert Lennox has been at my disposal, and it is not too much to say that but for his engineering skill, manipulative ability, and loyal perseverance, the present successful issue [liquefaction of hydrogen] might have been indefinitely delayed."

This appears to me to be a fair and true general statement of the case. In some quarters not friendly to Dewar it was suggested that Lennox was the mainspring of the whole enterprise. This I have always considered to be nonsense. Dewar had been interested in the liquefaction of gases before Lennox joined him. Great initiative was required to lay out the laboratory for this class of work, to decide on the general line of attack, and to secure the necessary funds.† It is fairly obvious that no one but a principal could really do this. Moreover, in talking to Dewar, and reading his writings, one could not fail to discover that he was a master of manipulative detail, and very fertile of resource. [I have gained invaluable hints from him in this way myself, coupled with a characteristic warning that I was not to repeat what he had told me to ——, though I might tell my Father.]

Notwithstanding what has been said above, Lennox's share was very important. He, it is believed, was mainly if not wholly responsible for the design of the compressors and liquefiers in their engineering aspect. By a rather curious arrangement they were made by a firm, Lennox, Reynolds and Fyfe of which he was the leading spirit. Their workshop was at Chiswick on the Thames, and Lennox himself lived there. But how he was able to find time for this while he was in regular attendance at the Royal Institution it is hard to understand. He must have relinquished all leisure and recreation. On one occasion he invited me to see the Oxford and Cambridge boat-race from his premises, but unfortunately I did not accept the invitation, and missed the opportunity of seeing his methods of work there, which, if I dare confess it, would have interested me very much more than the boat-race. Lennox's engineering enterprises were apparently not at first very successful from a financial point of view, and financial reconstruction had to be resorted to more than once. It is probable that his duties at the Royal Institution prevented his giving adequate attention to the business. The large air pumps used in Dewar's laboratory for evaporating liquid air and liquid hydrogen *in vacuo* were of his design and construction. They were of the rotatory type with an eccentric barrel and sliding feathers,

* A further idea of Lennox's personal appearance may be gained from the picture by H. Jamyn Brooks at the Royal Institution, representing one of Dewar's lectures on liquid hydrogen (1904). His is the bearded figure at the back partly turned away from the spectator, and handling an electroscope; No. 141 on the key plate, though his name is not given there.

† In the early days the cost of liquefying hydrogen was estimated at £20 for material each time. But of course the expense was mainly in installing the plant. In those days the whole idea of scientific equipment costing thousands of pounds was unfamiliar (except perhaps in connexion with astronomy) and such funds were not easy to raise.

and so far as I know they were the first successful air pumps of this design, though the fundamental idea as applied to water pumps is a very old one.* Improved air pumps of this kind have since been introduced by Gaede and others.

The personal relations between Dewar and Lennox struck me as very strange. Lennox admired his chief and, so far as I know, his way of referring to him was always respectful and decorous. But behind the scenes it was very different, and plain speaking on both sides was the order of the day. Indeed, I have been in the laboratory while delicate manipulations were in progress and whenever Dewar made a suggestion as to how some particular operation should be carried out, Lennox apparently made it a point of honour to contradict him, and to do something different. So far as I could observe this *riposte* did not generate any ill feeling, the parties understanding one another well, and finding it rather stimulating than otherwise.

On other occasions I believe it went further, and really high words passed. It was suspected by a favourably placed onlooker that if Lennox considered that too much had been said, he saw to it that the machinery should not be in working order when liquid hydrogen was next wanted. Many such quarrels subsided, each party really having a great respect for the other, and each being unwilling to bring the fruitful co-operation to an end. Finally, however, in 1908 the end came. It appears that an expensive plant designed and made by Lennox for the separation of helium from the Bath gas by rectification failed almost completely. Dewar complained in no measured terms, and Lennox as usual made his reply. If they had limited themselves to words the breach might have been healed: but they started exchanging angry letters, and a permanent quarrel resulted. Both regretted this when it was too late, but neither would make any advance, and Lennox never came near the Royal Institution again until after Dewar's death in 1923. Then he took an early opportunity of resuming the connexion, of which he had been very proud, by becoming a member.

Lennox's skill in laboratory arts was great, and he had that courage and confidence in his own ability to carry out any operation which goes so far towards assuring success. The early vacuum vessels devised by Dewar were made by him without any special appliances beyond an ordinary laboratory blowpipe and his two hands. Some of these historic vessels may be seen at the Royal Institution. He had a great belief in the importance of being in good form for such work, and when he felt himself to be so, no difficulty would daunt him. I have seen an enormous tubular vacuum vessel part of the helium liquefier, which, I was told, was made by Lennox using an oxygen blowpipe, with three men handling the glass under his directions. The manufacture of such things had then not been commercially organized and the machines which now make it comparatively easy did not then exist.

Lennox was gifted with a somewhat cynical sense of humour. Thus, he was preparing hydrogen for use in a hydrogen thermometer to determine the boiling point of liquid hydrogen and some criticism was made as to a possible presence of air in

* See reference (9). Young makes reference to Ramelli, who wrote as early as 1588.

the gas. "Well," said Lennox, "never mind that. It will make the temperature come all the lower."

Again, he was interested in an acid-resisting iron alloy. The peculiarities of this had apparently been noticed by a workman, who remarked in surprise "t'aint iron". From this incident the trade name of Tantiron was adopted. "It is curious", said Lennox, "that so many analysts should find tantalum in it."

Lennox was not fortunate in some of the happenings of his life, but his character was stoical in the extreme, and no blow of fate seemed to have any effect on his iron composure. A serious accident occurred when he was trying the generation of acetylene under pressure, with a view to storing it liquid in cylinders. There was a violent explosion. Sir Joseph Petavel was in the next room. The first thing he heard after the explosion itself was Lennox's voice saying "Look out, you men, put out the gas in there." Next, he saw Lennox, his face streaming with blood and one of his eyes was torn to pieces and the fragments spread all over his face, but quite calm. His first thought had been to prevent any further accident from the escaping acetylene. He always seemed quite indifferent to personal danger, and remarked that his old schoolmaster had been accustomed to say that a man born to be hanged would not come to any other end.

Again, in 1926, he came to see Sir Joseph Petavel at the National Physical Laboratory. He said that the doctors had given him three months to live and that they were probably right. Petavel tried to say something to raise his spirits, but he brushed this aside, saying that everyone had to die, and showing no signs of being in any way moved at the prospect. The doctors proved to be right, almost to the day.

Under Lennox was Robert Johnson, who went to the Institution in 1892. Dewar used to refer to him as "my old gasfitter", but he was in fact a competent mechanic, with considerable powers of leadership, great personal strength, and skill in making the best use of it. With the help of three or four men he would take down one of the compressors, repack the pistons, and have it ready for use again in less than an hour. He had a modest pride in his work; I remember, for example, cross-examining him about his methods of making soldered joints in pipes, and in reply to something I said about the difficulties of getting them tight, he remarked that there had not been any complaint of the joints since he had been there. Though he cannot have understood much of the scientific aspects of the work, yet he entered into the spirit of it as far as he was able, and expressed to me his pleasure in the liquefaction of hydrogen. "It comes out so clear", he said.

Like Lennox, Johnson was absolutely unsparing of himself, and it was hardly realized until his course was nearly run out that anything was amiss with him. One day he was working on one of the machines with a spanner, when Dewar noticed a lesion on his arm, and, always kind and solicitous as he was about matters of health, sent him off at once to a consultant physician to be examined, though apparently without fully realizing how serious the trouble was. Johnson put on his pilot jacket, and set off along Albemarle Street, with his square thickset figure and sturdy rather groom-like walk. It was for the last time. In ten days he was dead of "galloping consumption".

A bearded figure, well known to all habitués of the Royal Institution, is seen on the lecturer's right in Jamyn Brooks's picture,* ready to hand the pointer for wall diagrams and to switch off the lights for any demonstration requiring darkness. He was universally known as "Richard". No one at the R.I. ever used any other name—I find, however, on enquiry that his patronymic was Fowler. By training, he was a carpenter, and a good one. He came from Yorkshire, and had the independence of character which is usually associated with that part of the country. His politics were conservative and if he was moved to make a remark on subjects of public interest, it would often be to express satisfaction at a conservative victory at a by-election, or something of the kind. He had been under Tyndall, who, he told me, was an exacting master. It was amusing to see his relations with Dewar. Richard had commonsense backed by a good deal of quiet obstinacy, and if he had a point of his own he would stick to it with a minimum of words. If Dewar spoke sharply to him, he made it very obvious that he was not impressed. His capacity to stand up to so formidable a personality made him somewhat of a hero in the eyes of the younger members of the staff.

One of "Richard's" functions on Friday evenings was to make his appearance at the door when the clock struck nine, to summon the board of managers and the lecturer to enter. Rather an elaborate ritual was observed on these occasions, the lecturer entering closely attended by Dewar. Sir Charles Wheatstone, it used to be related, when about to give a Friday Evening Discourse, found his nerve fail him at the last moment, and bolted. Faraday, though, of course, quite unprepared, saved the situation by giving an impromptu lecture. I believe it was that afterwards printed as "Thoughts on Ray Vibrations"[10]†. Dewar often referred to this incident, and told the lecturer of the evening that it would not be allowed to happen again.

Another vignette is at the time of Queen Victoria's Diamond Jubliee (1897). Everyone put up some kind of illumination on their houses, but the Royal Institution (where the electric arc was originally discovered by Davy) had something in character, by putting up an enormous naked arc on the roof. It was struck by a supplementary carbon rod, and hand-tended, and it took so large a current as to cause a serious fall of voltage in all the neighbouring houses. It was conspicuous all down Albemarle Street, and I have the mental image of a drunken man in the street, staring up at it, and shouting "put out that light".

§ 4. SIR WILLIAM CROOKES, O.M., 1832–1919

Sir William Crookes‡ was a scientific worker typical of an epoch that has passed away. He was, I think, essentially of the school of Faraday. Like Faraday, he was of somewhat humble origin, and largely self-taught. Like Faraday he was skilful in experimental technique, and relied mainly on his own intuition rather than on any

* No. 139 on the key plate.

† Faraday says, p. 349: "I do not think I should have allowed these notions to have escaped from me, had I not been led unawares and without previous consideration, by the circumstances of the evening on which I had to appear suddenly, and occupy the place of another."

‡ I call him so throughout, but his knighthood dated from 1897.

very definite reasoning to guide him as to the subjects to be taken up: and like Faraday he was without the measure of mathematical training that is now expected from every serious student of physics or physical chemistry. When he was in his prime, an equipment of this kind was by no means inadequate, as Crookes's own career very clearly proves; and it may be suspected that even now, too keen a critical faculty, and too much knowledge of what has been done by others, is not always an unmixed advantage to one who aspires to be a pioneer in new fields.

It was a favourite remark of Lord Kelvin that Crookes had started more absolutely new hares than any other man among his scientific contemporaries. One of the most notable, the radiometer, made its appearance at a time when scientific sensations were not so frequent as they have since become, and it excited a widespread interest. Radiometers were to be seen in the shop windows of chemists and opticians all over London, and in provincial cities as well. They were indeed calculated to excite the curiosity of almost anyone as they spun round vigorously in the sunlight. The chief scientific interest was aroused at first from the idea that the effect was directly due to the pressure of light, the existence of which had for long been thought probable. If this were so, the mechanical reaction of the pressure would be on the sun. When Schuster showed that the reaction was in fact on the glass bulb of the instrument much of the sensational interest evaporated. These events occurred about the time I was born: but as a boy I well remember the radiometer to be seen everywhere in the shop windows. The revolving vane was of course a toy, and of little use as a measuring instrument, but torsion radiometers have been developed as delicate detectors of radiant energy by E. F. Nichols and others.

My first visit to Crookes's house was in 1896, in company with my Father; Crookes had seen the early experiments on the isolation of argon, by removing the nitrogen from air by sparking with an induction coil, actuated by a primary battery and hammer break. He invited my Father to come and see his own electrical equipment, which he had found to be capable of oxidizing nitrogen with comparative rapidity, and kindly allowed me to come too.*

We were received by Crookes and his wife. Lady Crookes's interests were entirely of a domestic nature. She was wrapped up in her husband and family, and never tired of telling of their doings. She delighted to help him when she could, and, she told me, often carried out the weighings for him in his chemical work, work which, as she said, was suited to the delicate fingers of ladies. It was obvious how devoted Crookes and she were to one another.

We had lunch in the dining-room on the ground floor, where there was a full-length portrait of Crookes as a considerably younger man, with a golden yellow beard, standing beside a table on which was an induction coil, and holding a pocket spectroscope in his hand. By an odd freak of memory I recall a chocolate pudding which was so popular that there was not enough of it to go round.

During lunch our host told of a recent incident in connexion with the water analyses which he carried out in collaboration with Dewar for the various London

* His house was No. 7, Kensington Park Gardens, not far from Paddington Station. This was not the scene of all his best known researches. He had moved there in 1880.

water supply companies of those days. The analyses from the supplies which came into London from different directions showed a remarkable similarity. Suspicion was aroused. The man whose duty it was to take the samples was "shadowed" and it was found that he filled up all the sample bottles from the same tap! As a natural result he was, as Crookes expressed it, "presented with the sack".

After lunch we went up to the library on the first floor. This was the best room in the house. There was a drawing-room for Lady Crookes to receive her friends, but it was on the ground floor, and I never penetrated to it. The library was lined with books, and there were various objects of scientific interest distributed about as ornaments: for instance a cut slab of meteoric iron; a shield-shaped piece of Labrador spar over the fireplace; and the largest radiometer I have ever seen. There were various mahogany cabinets containing specimens and under a glass shade an apparatus which had been used by Faraday in supporting specimens to be tested for dia- or para-magnetism. This, he told us, he had brought away from the Royal Institution when he had gone there to give a lecture. I think he had actually seen Faraday using it. The room was comfortable and well furnished, and everything in it was scrupulously tidy. No papers were lying about. They were all carefully filed: and there were neat box files on the shelves containing off-prints of scientific papers. I have never seen a more orderly man than Crookes. He never scribbled memoranda, or labels, and he never put anything away except in its proper place. There was an entire absence of litter in his library or his laboratory, and this result was not, as in some other cases, a symptom of inactivity.

Crookes did all of his correspondence, which was extensive, at a typewriter (fig. 6). He must, I imagine, have learnt to use it with facility late on in life, for typewriters can hardly have been available when he was young.

We went into the laboratory which consisted of a suite of rooms on the same floor as the library. There was a physical laboratory (fig. 7), which had the same general air of tidiness as the library, with glass cases containing many radiometers and vacuum discharge tubes. Seeing me examining these, Lady Crookes remarked: "We have not nearly so many of them as we had. The ex-emperor Pedro of Brazil came to see us, and asked for many of the best ones, and Mr Crookes did not see how he could refuse." I told this afterwards to my Father—and he said he thought that he personally would have refused!

The physical laboratory was rather restricted for space, and such space as there was was largely occupied with fixtures, so that it would to all appearances have been difficult to find room for working on any other class of problem than the high vacuum and electric discharge work which Crookes had made his own.

Crookes had almost inevitably been concerned in the development of the electric lamp industry, and his assistant Gimingham who had helped him in his well-known researches on the radiometer and on "radiant matter" (kathode rays) and who had acquired skill in glassblowing and vacuum technique, afterwards went into the young electric lamp industry, and no doubt assisted materially in its birth.*

* The glass globes used by Rayleigh in his weighing of gases, which led later to the discovery of argon, were made under Gimingham's supervision.

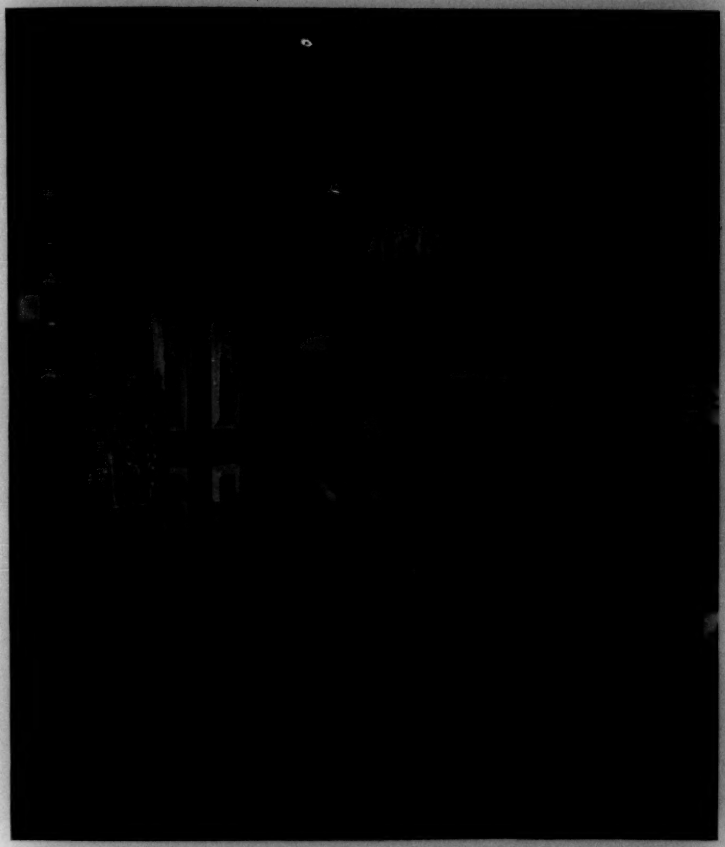

Figure 6. Sir William Crookes in his library.

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Crookes showed us some of his work, including an electric lamp bulb which he described as the smallest in the world: I am not sure however that it would have impressed the rising generation so much as it did us. They might remark that they could buy torch lamps as small or smaller for a few pence at Woolworth's Stores! I also noticed, on the wall of the laboratory, what one might regard as the parent of the modern neon signs—a vacuum tube bent to spell the word "electricity". Needless to say, it was not charged with neon, which was only discovered some years later. Crookes had been one of the first to light his house electrically, and I have read somewhere that the wires were carried under the floor, insulated in glass tubes.* I learn from Mr Gardiner that the lamps were run direct from a dynamo driven by a gas engine, the plant being situated in a cellar dug out from the space on one side of the front door.

One of his reminiscences about the early development of lamp making was that women workers had been introduced to do the glassblowing, which in those days was done entirely by hand, the bulbs being blown from tubing. The girls at first wore their hair in an elaborately curled fringe across the forehead, in accordance with the prevailing fashion. However, if one of them ceased for a moment to work the foot bellows while her head was bent over the blow-pipe, the loose smoky flame rose up, with disastrous results to the fringe. As may be supposed, fringes did not continue to be worn in the factory for very long under these conditions.

The primary object of our visit was for our host to show us the oxidation of nitrogen, using his own plant which consisted of a motor-alternator, placed underneath the window frame so as to have the direct support of the wall, and a large induction coil of Apps' make, which he had used for his researches on high vacua, and which (I believe) is now in the Science Museum. This was used as a transformer. The arc discharge itself was surrounded by a loose flame.†

Crookes had it enclosed in a glass globe, in which the red colour of nitrous fumes soon became apparent. When the globe stood over alkali, absorption occurred almost immediately.

Crookes showed us casually an interesting experiment which, by way of a diversion, I will repeat for you now. Glass rods are attached to the terminals of the induction coil, and, if I warm them, to make them conducting, you see that the flaming discharge passes as well from these glass terminals as from metal ones.

Beyond the main (physical) laboratory were other rooms. One of them was a small workshop, containing a Pittler lathe, and a small shaping machine, blow-pipes for glass working, and so on. The other was a chemical laboratory, where had been carried out Crookes's elaborate fractionations of the rare earths. His work in this

* The first electric installation I personally saw was that put up by the late Lord Salisbury at Hatfield House. Round the gallery of the library, simple cotton-covered insulated wires were carried in full view. A man had (somewhat inexplicably as it now appears), been killed by accidentally touching a live wire at a moderate voltage during the erection of the plant. I was about seven years old and a young girl cousin and I toyed deliciously with our fears by touching the cotton-covered wires. As the current was not on, the danger was perhaps not so great as we supposed. This was in 1882.

† Many years ago I showed that this "flame" is identical with the afterglow observed in vacuum discharges. It is possible to pass continuously from the former to the latter. The flame, like the afterglow, is due to the oxidation of nitric oxide by ozone. See reference 11).

direction must have involved immense labour, and he told me a little after this time that, though he hoped to glean a few more facts, he did not expect to see anything approaching finality. Indeed, it is doubtful whether these problems could ever have been satisfactorily resolved without the help given by X-ray spectra, which only became available much later. Crookes was at one time inclined to the view that in the rare earth group there were numerous elements differing from one another almost insensibly; and his speculations on this subject could plausibly be represented as heralding the modern conception of isotopes. However, as time has shown, they had not in reality a sound experimental basis.

To me personally, as boy and man, Crookes was most kind and friendly. Knowing me to be keenly interested in vacuum tube work, he asked his assistant, Mr Gardiner, to make a cathode ray tube for my instruction. Some yttria was treated with strong sulphuric acid and ignited. It was placed in the discharge tube, and highly evacuated with the Sprengel pump. Looking back over the years with some experience of such matters gained in the meantime, the whole technique seems to me to have been most efficient, and carried out in a wonderfully short space of time. No doubt the appliances then available were poor, judged by modern standards, but it was striking to see what they could do in skilled hands. The yttria under cathode ray bombardment shows the characteristic "citron band" spectrum which Crookes had discovered, and which enabled him to prove the presence of yttrium in all kinds of calcareous materials. I have the tube still, and have brought it to show you.

It was a source of great annoyance to Crookes that he had missed the discovery of the X-rays. According to the account he gave in my hearing, he had definitely found previously unopened boxes of plates in his laboratory to be fogged for no assignable reason, and, acting I suppose in accordance with the usual human instinct of blaming someone else when things go wrong, he complained to the makers, who naturally had no satisfactory explanation to offer. I believe it was only after Röntgen's discovery that he connected this with the use of highly exhausted vacuum tubes in the neighbourhood. He had, at least, less to reproach himself for than another English man of science, who, it was said, knew that high vacuum discharge tubes were apt to fog photographic plates anywhere near them, and only drew the moral that the plates should be stored elsewhere.

Crookes' first visit to South Africa was in 1895, just after the Jameson Raid. He had gone out to give evidence in a patent litigation. After the South African War, he and the late Lord Haldane were appointed to sit with my Father on the Explosives Committee of the War Office, designed to make good some of the deficiencies which the war had revealed. They came to Terling to discuss preliminaries with him. This was in June 1900. My Father did not like the smell of smoke, but Haldane was an inveterate smoker of cigars, and as deputy host I sat up with him and Crookes in the smoking-room. The conversation turned on South Africa, and Crookes spoke of his visit to Pretoria, and his interview with President Kruger on the latter's verandah, or stoep, decorated with the well-known stone lions. One of the things that seemed to have impressed him strongly was the disreputable ap-

Figure 8. Sir William Crookes in his chemical laboratory.
(Near the end of his life)

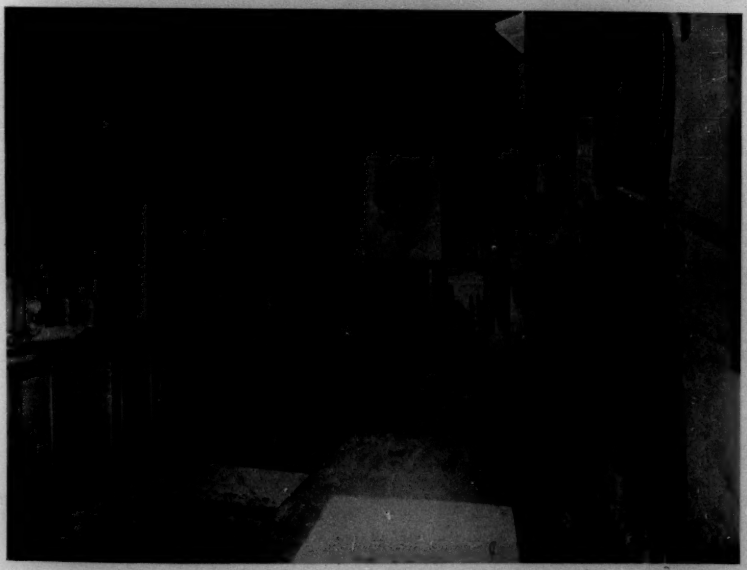

Figure 7. Sir William Crookes's physical laboratory.

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pearance of the Presidential tall hat, which he said was worse than anything he could have imagined. On the question of the Uitlanders and their political rights Kruger represented that all difficulties between them and the Boers would settle themselves in the course of a generation by inter-marriage. This seemed plausible enough at first hearing, but, on learning more of the subject from other sources, he found that all that the President had told him was "a pack of lies". It must be remembered that this conversation was held too soon after the war for a very tolerant or judicial attitude to be possible.

Another of Crookes's anecdotes shows him as a man of action. He had had a difference with a business partner, and the partner refused to give up certain documents to which Crookes laid claim. These, he had reason to believe, were in a city office [I suppose belonging to the partners jointly] of which the other partner was in possession. Having sought legal advice, Crookes proceeded to the office in the early hours before anyone was about, taking a locksmith with him. The lock was forced, and the documents recovered.

Crookes was deeply interested in the properties of the diamond, and in the peculiarities of individual diamonds. He was in touch with the De Beers Company, and I well remember the contempt with which he spoke of the action of "our precious government" in driving the company's headquarters from London to South Africa, as a result of income tax regulations. He had early observed the brilliant phosphorescence of some unusual diamonds under cathode rays, or "radiant matter" in his own phrase. Later, he repeated the experiments of Moissan on the artificial production of diamonds in the electric furnace, and considered that he had confirmed the results. However, after Crookes's death, the hard crystals which he had obtained came into the hands of Sir Charles Parsons, who was unable to induce them to burn in oxygen, and concluded that Crookes's identification of them as diamonds was mistaken.

Crookes experimented too, on the coloration of diamonds by radium rays. He produced some beautiful specimens of coloured stones in this way, and was in the habit of wearing a green diamond so coloured set in a ring.

It would not be fair to call Crookes a secretive man: nevertheless a certain sense of reserve was apparent to those who attempted to press him for information on scientific subjects. One well-known authority on electric discharge phenomena told me that he had given up asking Crookes questions—not because information was refused, but because he had a feeling that it was not willingly given. I remember at a later visit to his laboratory, Crookes generously showed me his unpublished investigation of uranium X, the first disintegration product of uranium, which afterwards became classical. He introduced it by saying that he had no objection to showing me a research which he had in hand. I was somewhat surprised by this turn of phrase, as it had never previously occurred to me that a scientific man could be unwilling to open his mind freely about matters like this, which had no commercial application. Crookes had done a good deal of commercial scientific work, being indeed dependent on it for an income, and possibly the attitude I have referred to may have been cultivated in connexion with it. He was also a good deal in

demand as an expert witness, and his name carried deserved weight, but, as a distinguished lawyer has told me, it was not much use to press him closely as to the logical implications of what he had said. He was an admirable experimentalist and a good man of business, but not a logician.

Looking over old letters, I find one from Crookes that contains some practical wisdom, and seems worthy of reproduction.

7, KENSINGTON PARK GARDENS,
Nov. 14th, 1907.

Dear Mr Strutt,

Rutherford asked me to exhibit something at the Franco-British Exhibition, and I told him I really had nothing I could show. You ask me for an original spinthariscope. All my original ones were given away years ago, and now, when I want one I go to Beck's or Cossor's and buy one. But if I had anything to exhibit I doubt if I should be willing to do so. My experience is that an immense amount of trouble and some expense is involved. A case has to be provided, and fittings, labels, etc. got ready. Then the things to exhibit are so small that no one sees them. Scientific exhibits are of no interest to the public and men of science can see the same things far better elsewhere. Exhibitions are for large scale purposes. Had I a steam engine or a dynamo to show, I should send my men to put it up and take all the trouble, but here I have to do it all myself, and I really have no time to spare. I have some investigations half through, and I want to spend as much time in my laboratory as possible to get on with them.

I hope you will understand my position. You...with half a century in front of you can afford to be lavish of time, but I with my half century behind me, and naturally only a few years in front, must be parsimonious.

Believe me,

Very truly yours,

WILLIAM CROOKES

Mention has already been made of the joint work of Crookes and Dewar on water analysis. Crookes was a man of courteous and conciliatory manners: and I remember John Perry, one of our former Presidents, remarking that no one could possibly quarrel with him. Nevertheless Dewar accomplished the feat, and the partnership was, I suppose, dissolved. Both Crookes and Dewar were connected with the Royal Institution, the former as secretary and the latter as Fullerian Professor of Chemistry and director of the laboratory. There was therefore an *impasse*, and Crookes placed himself in the hands of the Duke of Northumberland as President of the Institution. The Duke took the view that as Crookes was to be President of the Royal Society, he could stand back without loss of dignity, and at the Duke's request he did so, though not very willingly. So far as I am aware, Crookes was never able completely to forget or forgive. But whatever his feelings may have been, he did not allow them to influence his actions. As President of the Royal Society he brought forward Dewar's name for the Society's greatest honour—the Copley Medal—and drew up a statement of Dewar's scientific merits in support. This was written with great care so as to do strict justice, without being in any way fulsome. The concluding sentence ran:

"The Nation owes Sir James Dewar a debt for his contributions to natural knowledge, and this debt the Royal Society will fitly recognize by conferring on him the Copley Medal."

Shortly after the declaration of war in 1914 Crookes brought forward a method of secret night signalling which he had worked out in collaboration with his assistant Mr Gardiner and which consisted in putting in or taking out a weak didymium glass from in front of a source of light. The general opacity was not enough to diminish the light appreciably, and it was not apparent to the naked eye that any change had been made, but anyone in the secret who watched with a direct vision prism, could readily observe the appearance and disappearance of the most conspicuous absorption band. I never heard that any use was made of this idea in practice, and it is perhaps chiefly interesting as showing the inventiveness of a man of eighty-two years of age, and his desire to do something for his country.

During the War Crookes served as a member of the Admiralty Board of Invention and Research. He was always treated with especial courtesy and consideration by Lord Fisher, the chairman, as was indeed fitting in view of his age and position. It cannot be said that he contributed much to the proceedings, and his activity was diminishing. But he went on to the end, his last paper appearing in his eighty-seventh year. He died while it was passing through the press.

I am indebted to Mr Gardiner for the photographs reproduced.

§ 5. SIR ARTHUR SCHUSTER, 1851–1934

I have always understood that Sir Arthur Schuster met with some initial opposition from his father in following his strong natural bent towards physical science. The father's own interests were all in the direction of finance and commerce: and he was almost as much perplexed and distressed as the traditional hen which has hatched out a duckling and finds it determined to take to the water. He came to Sir Henry Roscoe and expressed his annoyance and disappointment. But Roscoe insisted that he was making a mistake and that if he would only let his son have his own way, he would soon be proud of him: and so it proved.

Roscoe indeed had great and well-placed confidence in him. When on the death of Balfour Stewart the professorship of Physics at Manchester became vacant, Roscoe was earnest in promoting Schuster's candidature. The late Lord Rayleigh was consulted, and Roscoe was almost indignant with him for expressing any hesitation between Schuster and another very strong candidate. "Why won't you say straight out that Schuster is the best?" he said.

Schuster was one of the now fast diminishing band who derived personal inspiration from Clerk-Maxwell. He used to deplore the fact that the rising generation of physicists did not study Maxwell's great book on *Electricity and Magnetism* at first hand, but were content to derive their knowledge from secondary sources. He forgot perhaps the demands made on the student by the ever-widening range of scientific knowledge, and the necessity for learning established doctrine in whatever way may be the easiest.

I learnt from Schuster an aphorism by Maxwell which is perhaps not on record,

and this opportunity of preserving it may be taken. Some question being raised as to whether a particular scientific communication was worth publishing, Maxwell remarked: "Whether it is worth publishing depends on what ratio the ingenuity it displays bears to the whole ingenuity of the author." This consideration may very naturally guide authors themselves; but referees and publication committees usually attempt to apply a more objective standard of merit.

The following from Schuster to Rayleigh (August 1st, 1909) is worth preserving:

"There is much in these letters [from Maxwell to Rayleigh] that is interesting. If opportunity offers I think the one dated December 6th 1871 is well worth publishing.* I dont remember the 'moral' of the 2nd law [of thermodynamics] being put in the way it is done in this letter. The description of the consequence of reversal of motion of every particle in the universe I have seen ascribed to Kelvin. It is put in this letter as something original. As regards this matter it would no doubt appear very grotesque to an outsider if he could see people imagining that they are getting older when they are really getting younger, but should *we* notice anything strange about it? If anyone was to assert at the present moment that this reversal has taken place, and that all our recollections are really prophecies, and *vice versa* is there anything to disprove it? Here is the foundation of a new philosophy."

Schuster's scientific career has been set out in adequate detail by Professor Lees, and I shall not attempt to recapitulate what has been so well told by him. Schuster's style was essentially addressed to academic readers, and even in his more popular writings such as *Britain's Heritage of Science* he made, and desired to make, no appeal to the gallery. His enthusiasm was not obviously aroused by skilful technique or by ingenious mechanical devices. I have heard him speak as if he considered the development of wireless telegraphy a very much overestimated achievement, when compared with Hertz's fundamental experiments on electric waves. For him, science consisted mainly in the discovery of scientific facts and laws, not in applying them to the service of man. So well-balanced a mind could not fail to understand how great are the difficulties which inventors have to overcome: but these triumphs were not the things in which he personally delighted.

Schuster was near making some of the most important discoveries of his day. Two instances particularly come to mind. He used to tell how in early days he looked for the effect of a magnetic field on spectrum lines, subsequently discovered by Zeeman. Having arranged the experiment, with his eye to the spectroscope, he turned on the electromagnet and observed a large broadening of the lines. At first his hopes were high. But further investigation showed that what he had seen was to be explained by the magnet pulling apart the steel jaws of the slit!

Again, he was perhaps the first to realize the important information that could be gained by a quantitative measurement of the deflection of cathode rays in a magnetic field. He carried out measurements of this kind himself, and drew provisional conclusions, but these failed of success through his having over-estimated the effect of the resistance of the gas on the motion of the particles. I once happened

* It is now published in *Life of Lord Rayleigh*, p. 47.

to be with Schuster looking at a demonstration of X-ray apparatus. He remarked: "I owe a heavy grudge to Röntgen's discovery. It came out just at the time when I was working at the magnetic deflection of cathode rays. I laid my work aside and devoted all the resources of the laboratory to making and exhausting X-ray tubes, and taking photographs for the hospital at Manchester. The result was that other people got in first with the discovery of the electron."

It may be that if he had been gifted with a somewhat more vigorous physique, he would have been able to push these investigations to ultimate success in both cases. It is clear that he had the root of the matter.

As Secretary of the Royal Society, Schuster always took a broad point of view about the scientific work on which it was his duty to form a provisional judgment. With his great interest in the history of science, he had taken to heart the lesson that the orthodox view is not necessarily right. Thus on one occasion when the views of the late Professor A. W. Bickerton of Christchurch, New Zealand, on "impact" had come up, Schuster characteristically remarked: "We must give the heretics their chance." He was quite prepared to consider with an open mind the alleged phenomena generally called "spiritualistic", but modestly doubted his own capacity to detect trickery.

He thought that scientific bodies should not attempt to restrain men of established position from expressing any views they pleased. That, he considered, was outside their proper function. "If", he would say, "a man of standing chooses to make a fool of himself, that is his own affair, and I do not see that it is anyone else's business to stop him." When, late on in his life, a paper of his own was criticized by a referee, he took the view that at his age he had earned the right to say what he liked. He considered that the system of the French Academy of Sciences, which allots, as of right, a certain amount of space to each of its members, was worthy of imitation.

In the early phases of the war, the hysterical outbreaks of spy mania made difficult the position even of British subjects of long standing who had been born in Germany. Schuster was one of the sufferers, and the fact that he had installed at his house a wireless receiving set for getting the time from the Eiffel Tower station* gave a handle for the most grotesque misrepresentations. Attempts were even made to eject him from his position as Secretary of the Royal Society, but his friends stood by him, and, so far as can be judged, these attempts fell far short of success. To Schuster, however, all this came as a rude shock. Conscious of a life's work spent with complete loyalty in the service of the intellectual life of this country, it had not occurred to him that anyone could be so perverse as to take a different view: and when the ferment had subsided, he was not able to forget what had passed.

As a man of science, Schuster was singularly fair minded and unprejudiced. To the end of his life he remained free from the inflexibility of opinion which is so often the penalty of old age. For example, I ventured to ask him whether he still adhered to the opinion expressed in the preface to his *Optics* (1904), "Those who

* This was, of course, before the days of broadcasting, and wireless receiving sets were not in general domestic use.

believe in the possibility of a mechanical conception of the universe, and are not willing to abandon the methods which, from the time of Galileo and Newton, have uniformly and exclusively led to success, must look with the gravest concern on a growing school of scientific thought which rests content with equations representing numerical relationships between different phenomena even though no precise meaning can be attached to the symbols used." "No," he replied, "I do not see how one can stand to that any longer."

Throughout a great part of his life his health was not very firm, though so far as I know he was not put out of action by long illnesses. He remarked once to me that he found that he could give an elementary lecture better when he had a slight headache, because that removed the temptation which he otherwise felt of allowing his mind to run on to other matters.

Even in hours of relaxation, the subjects on which he chiefly liked to dwell were science and the personalities and idiosyncrasies of scientific men. Politics hardly seemed to interest him at all, and he made no effort to join in when such subjects were under discussion. During his holidays he made charming water colour sketches which he would show with some legitimate pride to his friends. His interest in Art extended considerably beyond the range of that branch of it which he himself practised. But there I was not very competent to follow him. I remember his pleasure in a large piece of Della Robbia ware which was over the door of his dining-room at Manchester.

Schuster was a man of somewhat reserved exterior, and had a sensitiveness that would, perhaps, scarcely have been suspected by those who only knew him slightly. But beneath these characteristics lay a warm heart, and a capacity for sincere friendship. Towards the end of his life, when his health had finally given way, he said that to find himself remembered by his old friends was the only pleasure that remained to him.

Here I will bring this instalment of my recollections to a close. It would have been easy to cover a wider field: but I have preferred to exhaust a few topics rather than to touch lightly on many. If I have been able to communicate a part of the interest which I have found in recalling them, it will be an ample reward.

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ON THE DETERMINATION OF VISCOSITY BY THE OSCILLATION OF A VESSEL ENCLOSING A FLUID: PART I

By Professor E. N. da C. ANDRADE, F.R.S.,
AND
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ABSTRACT. The method of measuring the viscosity of a liquid by observing the damping of torsional oscillations of a sphere containing the liquid was originally put forward by Helmholtz and Piotrowski. The form in which they carried out and calculated their experiments is ill adapted to give good results, and actually led to false conclusions. A disposition of apparatus and a method of calculation are described which can be made to yield accurate results. This has been checked by determining the viscosity of water over a range of temperatures.

§ 1. INTRODUCTION

The usual method of determining fluid viscosity is based upon the flow through some form of tube. It is suitable for such substances as organic liquids at the limited range of temperatures in which determinations are ordinarily made, but for substances such as liquid metals, which react with air, and for temperatures either above or below the ordinary range, it possesses many disadvantages.

The apparatus which must be maintained at a constant temperature is relatively large, and any speck of oxide which may become lodged in the tube leads to grave errors. The usual procedure is to use gas pressure to reset the liquid for each flow, although K. Spells[1] has recently designed an apparatus in which the flow method can be used without contact between gas and liquid metal. The necessity of observing by eye the passage of the liquid past fixed marks is another feature of the method which leads to complication.*

The only other method which seems to have been used for liquid metals is that of the damping of an oscillating body, e.g. a disc immersed in the liquid, as applied by Fawsitt[2] and, more recently, by V. H. Stott[3] to the measurement of the viscosity of molten tin. This method, which is not absolute but only comparative, suffers from many disadvantages, of which the effect of the surface of the liquid on the rod connecting the suspension system to the disc may be particularly

* Practical difficulties arise in the use of electrical contacts. See K. Spells[1].

mentioned. In general, it does not appear to be very well adapted for even comparative measurements.

A method which offers advantages is that originated by Helmholtz and Piotrowski[4], to which Dr Barr[5] refers as being "at least of historic interest". A sphere filled with the liquid is attached to a bifilar suspension and allowed to execute oscillations about a vertical axis. The logarithmic decrement is observed, and from this, and the constants of the apparatus, a value can be calculated for the viscosity. The original paper is certainly not such as to encourage others to use the method.* The calculations there given are very complicated and troublesome and the results very unsatisfactory. It was concluded by Helmholtz and Piotrowski that considerable slip took place between the liquid and the solid wall with which it was in contact, a result which has been quoted extensively, but is against the general experience of workers in this field[6]. The values found for the coefficients of viscosity differ, in one case very widely, from those now accepted—namely, 0·0157, 0·00251, 0·00360 for ether, alcohol and carbon disulphide at given temperatures in the neighbourhood of 20° C. as against the standard values, 0·0109, 0·00241, 0·00371 at the same temperatures. It is perhaps, therefore, not surprising that the method has not been extensively used. Ladenburg[7], however, repeated the measurements of Helmholtz and Piotrowski and was unable to find any evidence of slip; he himself obtained a value for water at 17·5° C. which differed by only 1 per cent from the standard value and a still better value at 19·2° C.

The method is so well adapted for measuring viscosities over a wide range of temperature on account of the ease with which relevant portions of the apparatus can be maintained at constant temperatures and with which the necessary readings can be taken, that we have devoted some attention to testing its validity and designing a form of apparatus suitable for the determination of the coefficient of viscosity to an accuracy of at least 0·5 per cent. It has been found possible to reduce the external damping—i.e. that which the oscillating sphere experiences owing to surrounding gas and the imperfect elasticity of the suspending fibres—so much that it can be practically neglected. This very much simplifies the calculation.

§ 2. CALCULATION OF THE COEFFICIENT OF VISCOSITY

The method of calculation adopted has been adapted from that used by Verschaffelt[8] for calculating the viscosity of a liquid gas from the damping of the oscillating of a sphere immersed in the liquid, and differs from that of Helmholtz in points that will be indicated.

The general equations of motion for a viscous fluid, summarized in vector notation as

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \operatorname{grad} \mathbf{v} = G - \frac{1}{\rho} \operatorname{grad} p - \nu \operatorname{curl} \operatorname{curl} \mathbf{v},$$

* "On voit combien ces rélations sont compliquées et quelle incertitude le calcul des expériences laissera planer sur la valeur de μ/f, qu'elles sont destinées à donner." Brillouin, *Viscosité des Liquides*, part 1, p. 102 (1907).

where $\mathbf{v}$ is the velocity, G the body forces, ρ the density, p the pressure and $\nu=\eta/\rho$ the kinematic viscosity, reduce to the form $\mathbf{v}, G, \rho, p,$

$$\left.\begin{aligned}\frac{\partial u}{\partial t}&=\nu\nabla^2 u\\ \frac{\partial v}{\partial t}&=\nu\nabla^2 v\\ \frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}&=0\end{aligned}\right\} \qquad \text{.....(1),}$$

on the assumption that the liquid moves in concentric spherical shells about the axis of rotation z, and that a given particle of liquid always remains in the same plane normal to the axis, i.e. that $w=0$, u, v and w being the components of velocity. u, v, w

We put $u=-y\psi, \quad v=x\psi,$ ψ

where ψ is a function of r, the distance from the centre of the sphere, and of t only, and we make the further assumption that r

$$\psi(r, t)=\phi(r)\, e^{\alpha t}, \qquad \phi$$

where $\alpha=-\beta+i\gamma$ .....(2). α

Here $\beta=\delta/T$, $\gamma=2\pi/T$, where δ is the logarithmic decrement and T is the time period. We then find for ϕ the equation β, γ, δ, T

$$\frac{d^2\phi}{dr^2}+\frac{4}{r}\frac{d\phi}{dr}=b^2\phi \qquad \text{.....(3),}$$

where $b^2=\alpha/\nu$ .....(4). b

The solution of equation (3) is

$$\phi=\frac{1}{r^3}\{A(br-1)\, e^{br}+B(br+1)\, e^{-br}\} \qquad \text{.....(5).}$$

So far we have given a very brief summary of the method of Helmholtz, to whom the reader is referred for details. Helmholtz proceeds from this point to find an expression for $\psi=\phi(r)\, e^{\alpha t}$ in terms of β, fixed by the damping; γ, fixed by the time period; σ and τ, which are functions of γ and β such that $\tau=\sqrt{(m/\nu)}\cos\epsilon$, m $\sigma=\sqrt{(m/\nu)}\sin\epsilon$, where $m=\sqrt{(\beta^2+\gamma^2)}$ and $\tan 2\epsilon=-\gamma/\beta$; and two complicated ϵ functions of r, denoted by C and C_1. Hence he gets the viscous force P on the C, C_1, P internal surface of the sphere in the form

$$P=Ke^{-\beta t}\cos(\sigma R+\gamma t+2\epsilon+\kappa),$$

where $K=\frac{8}{3}\pi\rho\nu R^4 C$ and κ (called δ_1 by Helmholtz) is a function of R, the radius K, κ, R of the sphere, introduced by a supposed slip between liquid and wall.

We then have the equation

$$I\frac{d^2\theta}{dt^2}=-f\theta-P-P' \qquad \text{.....(6),}$$

for the motion of the sphere, where P' is a term expressing the external damping P' (mainly air friction), θ is the azimuthal angle and f is the restoring force per unit θ, f angle of twist due to the suspension. This leads to

$$\eta=C/C_1 F,$$

F when F is a complicated expression in m, R, I and f. This expression for η is quite intractable, and to simplify it Helmholtz takes $C_1/C = \sqrt{(m/\nu)}$ which, it should be noted, is only true if the dimensionless quantity $\sqrt{(m/\nu)}\,R$ is very large, say greater than 1000. As the value of this quantity was only 7·5 in Piotrowski's experiments with water, the anomalous results obtained are not surprising. To find the constants in P' a separate experiment has to be carried out on the damping of the oscillations of the empty sphere. Finally, after a troublesome calculation, a value of η is obtained.

We desire to simplify the calculation and to avoid making any assumptions not compatible with practical experimental conditions. Under the conditions of our experiments it will be shown that the external damping is responsible for a very small correction only, and can be neglected in the first instance. We start with equation (5), and, having to consider conditions at the inner surface of the sphere, where $r = R$, neglect e^{-bR} in comparison with e^{bR}. To a first approximation the real part of b is, as will be shown later, $\sqrt{(\pi/Tv)}$—see equation (14)—which is not less than 3·6 in our experiments, while R for our smaller sphere is 2, so that the neglect is well justified. If the value of ϕ at $r = R$ is Φ, then

$$A = \frac{\Phi R^3}{bR-1}\, e^{-bR},$$

$$\phi = \frac{\Phi R^3}{r^3}\,\frac{br-1}{bR-1}\, e^{-b(R-r)},$$

and

$$\left(\frac{d\phi}{dr}\right)_{r=R} = \frac{\Phi}{R}\,\frac{b^2R^2-3bR+3}{bR-1}.$$

The angular velocity in any spherical shell is

$$\psi = \phi\,(r)\, e^{\alpha t},$$

so that

$$\frac{d\psi}{dr} = \frac{d\phi}{dr}\, e^{\alpha t},$$

and

$$(\psi)_R = \frac{d\theta}{dt} \qquad \text{.....(7).}$$

Supposing, in accordance with all modern experiment, that there is no slip between
χ liquid and wall, the viscous torque on an elementary zone, of latitude χ, measured from the equator, is

$$dP = 2\pi R^4 \eta \cos^3\chi \cdot d\chi \left(\frac{d\phi}{dr}\right)_R e^{\alpha t},$$

or

$$\begin{aligned} P &= 4\pi R^4 \eta \left(\frac{d\phi}{dr}\right)_R e^{\alpha t} \int_0^{\pi/2} \cos^3\chi \cdot d\chi \\ &= \frac{8}{3}\,\pi\eta\,\frac{R^4}{\Phi}\left(\frac{d\phi}{dr}\right)_R \frac{d\theta}{dt} \\ &= \frac{8}{3}\,\pi\eta R^3 \left(bR - 2 + \frac{1}{bR-1}\right)\frac{d\theta}{dt} \qquad \text{.....(8)} \\ &= L\,\frac{d\theta}{dt} \quad \text{say} \qquad \text{.....(8}a\text{).} \end{aligned}$$

L

If we put $L=M+iN$ and $b=g+ih$, then *M, N, g,*

$$\left.\begin{aligned} M&=\frac{8}{3}\pi\eta R^3\left\{gR-2+\frac{gR-1}{(gR-1)^2+h^2R^2}\right\}\\ N&=\frac{8}{3}\pi\eta R^4h\left\{1-\frac{1}{(gR-1)^2+h^2R^2}\right\}\end{aligned}\right\} \quad \text{.....(9).}$$

If there is no external damping, equation (6) becomes

$$I\frac{d^2\theta}{dt^2}=-f\theta-P \quad \text{.....(10).}$$

From equation (7) $\theta=\frac{1}{\alpha}\Phi e^{\alpha t}$,

so that $I\alpha^2+L\alpha+f=0.$

Substituting the value of α from equation (2) we have

$$\left.\begin{aligned} I(\beta^2-\gamma^2)-\beta M-\gamma N+f&=0\\ -2I\beta\gamma-\beta N+\gamma M&=0\end{aligned}\right\} \quad \text{.....(11),}$$

which gives

$$M=\beta\left\{\frac{f}{\beta^2+\gamma^2}+I\right\},$$

$$N=\gamma\left\{\frac{f}{\beta^2+\gamma^2}-I\right\}.$$

Remembering that

$$\beta=\delta/T,\quad \gamma=2\pi/T,\quad f=\frac{4\pi^2I}{T_0^2},$$

where T and T_0 are the periods of oscillation of the full and empty sphere respectively *T, T_0*

$$\left.\begin{aligned} M&=\frac{I\delta}{T}\left(\frac{T^2}{T_0^2}\frac{1}{\Delta^2+1}+1\right)\\ N&=\frac{2\pi I}{T}\left(\frac{T^2}{T_0^2}\frac{1}{\Delta^2+1}-1\right)\end{aligned}\right\} \quad \text{.....(12),}$$

where $\Delta=\beta/\gamma=\delta/2\pi,$ *Δ*

or to a good approximation, if Δ is small*

$$\left.\begin{aligned} M&=\frac{2\pi I\Delta}{T}\left(\frac{T^2}{T_0^2}+1\right)\\ N&=\frac{2\pi I}{T}\left(\frac{T^2}{T_0^2}-1\right)\end{aligned}\right\} \quad \text{.....(13).}$$

Equations (12) and (13) contain only measured quantities, so that M and N are known.

Now $$b=g+ih$$
$$=\sqrt{(\gamma/\nu)}\,(1+i)\,(1+i\beta/\gamma)^{\frac{1}{2}},$$

since $$b^2=\alpha/\nu=1/\nu\,(-\beta+i\gamma),$$

* In a typical experiment, with water at 12·7° C., δ was 0·04789, or $\Delta^2=5{\cdot}8\times10^{-5}$.

which gives

$$\left.\begin{aligned} g&=\sqrt{\frac{\pi}{Tv}}\left(1-\tfrac{1}{2}\Delta+\tfrac{1}{8}\Delta^2\right)\\ h&=\sqrt{\frac{\pi}{Tv}}\left(1+\tfrac{1}{2}\Delta+\tfrac{1}{8}\Delta^2\right)\end{aligned}\right\} \qquad \text{.....(14),}$$

neglecting Δ^3 and higher powers. To a first approximation

$$g=h=\sqrt{\frac{\pi}{Tv}}.$$

Referring to equations (9) which give η in terms of M and N (which have been found), g, h, and known quantities, we see that we have sufficient equations to find η, since g and h involve only η, T and ρ. However, since g and h contain $1/\sqrt{\eta}$, the exact evaluation of η gives a little trouble. This we can avoid by a method of successive approximations.

The quantity $(gR-1)^2+h^2R^2$, which occurs in equations (9), is large, being, e.g. about 80 for water near 0° C. with our smaller sphere, and greater in other cases. Hence, to a first approximation,

$$N=\frac{8}{3}\pi\eta R^4\sqrt{\frac{\pi}{Tv}},$$

or

$$\begin{aligned}\eta&=\frac{9N^2T}{64\pi^3R^8\rho}\\ &=\frac{9}{16\pi}\frac{I^2\,(T+T_0)^2\,(T-T_0)^2}{TT_0{}^4R^8\rho} \qquad \text{.....(15).}\end{aligned}$$

In the value for M given by equations (9) let

q

$$q=\frac{gR-1}{(gR-1)^2+h^2R^2} \qquad \text{.....(16),}$$

which is of the order 0·04. The value of gR is of the order 15, so that q is only a small correction, and the value of η given by equation (15) can be used to find its value. We then have, from the equation for M in equations (9),

$$(2-q)\,\eta-\sqrt{\frac{\pi\rho}{T}}\,aR\sqrt{\eta}+\frac{3}{8}\frac{M}{\pi R^3}=0,$$

or

$$q'\eta-\sqrt{\frac{\pi\rho}{T}}\,aR\sqrt{\eta}+\frac{3}{4}\frac{I\Delta}{R^3T}\left(\frac{T^2}{T_0{}^2}+1\right)=0,$$

q', a where

$$q'=2-q, \qquad a=1-\tfrac{1}{2}\Delta+\tfrac{1}{8}\Delta^2.$$

Hence

$$\sqrt{\eta}=\frac{aR}{2q'}\sqrt{\frac{\pi\rho}{T}}\{1-(1-\mu)^{\frac{1}{2}}\},$$

μ where

$$\mu=\frac{3q'I\delta}{2\pi^2a^2R^5\rho}\left(\frac{T^2}{T_0{}^2}+1\right),$$

or

$$\eta=\frac{a^2R^2}{4q'^2}\frac{\pi\rho}{T}\{1-(1-\mu)^{\frac{1}{2}}\}^2 \qquad \text{.....(17).}$$

While equation (15) should apparently give η within a few per cent, as far as the approximations made are concerned, actually $(T-T_0)^2$ is the main source of error, since T and T_0 are nearly equal. Owing to this, the first approximation for η may be in error by 30 per cent or more. The effect of this will be to render this value given by equation (17) in error by 1 or 2 per cent. It is then, however, only necessary to use this new value of η to find q', and to work through equation (17) again with the new value of q'. This stage of approximation gives η correct to well within the limits dictated by the various experimental errors. The third approximation is very quickly carried out, as the values of all the quantities involved in equation (17) except q' have been already calculated in the second approximation. In an actual series of experiments, and in finding the temperature coefficient of viscosity, it is generally possible to guess the first value of η to within a few per cent, instead of using equation (15); if so, the second approximation gives the required accuracy.

As an example we may take an experiment carried out on water at 13·4° C.

$$\delta = 0{\cdot}11236, \qquad I = 927{\cdot}14 \text{ g.cm}^2,$$
$$\rho = 0{\cdot}99935 \text{ g./cm}^3, \qquad T = 15{\cdot}113 \text{ sec.},$$
$$T_0 = 14{\cdot}719 \text{ sec.}, \qquad R = 2{\cdot}544 \text{ cm.}$$

With those values equation (15) gives

$$\eta = 0{\cdot}0171, \qquad g = 3{\cdot}487,$$

and we find

$$q' = 1{\cdot}943, \qquad \mu = 0{\cdot}6044,$$

from which equation (17) gives $\eta = 0{\cdot}01176$ as a second approximation, which differs so much from the first approximation that a third approximation is necessary.

Putting $\eta = 0{\cdot}01176$, we get

$$g = 4{\cdot}2020, \qquad q' = 1{\cdot}9534, \qquad \mu = 0{\cdot}60746,$$

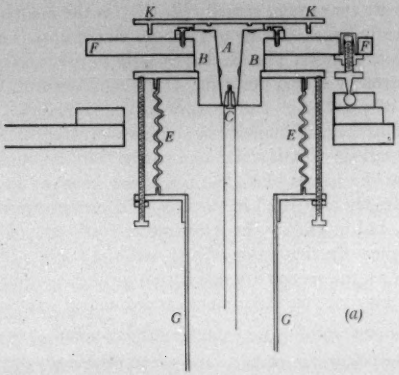
from which equation (17) gives $\eta = 0{\cdot}01207$.

To show how unnecessary it is to proceed further it may be mentioned that the effect of a fourth approximation is to give $\eta = 0{\cdot}012068$, instead of 0·012069 given by the third approximation.

§ 3. APPARATUS

The suspension was a bifilar one, which has obvious advantages. The first difficulty is that of obtaining a pure rotation, free from any swing. After electromagnetic methods of starting the oscillation had been tried, a mechanical arrangement was finally adopted.

The suspension head, shown in figure 1, consists of a truncated cone *A* fitting into a cylindrical block *BB*, which is fixed to a levelling table *FF*, the levelling screws being of the type used in the standard dumpy level. The cone was turned in the lathe so that the flat top was accurately normal to its axis, and at the same time a small coaxial conical hole was turned in the small end of the cone. When the suspension wires are fixed at opposite ends of a diameter of this hole, by means of



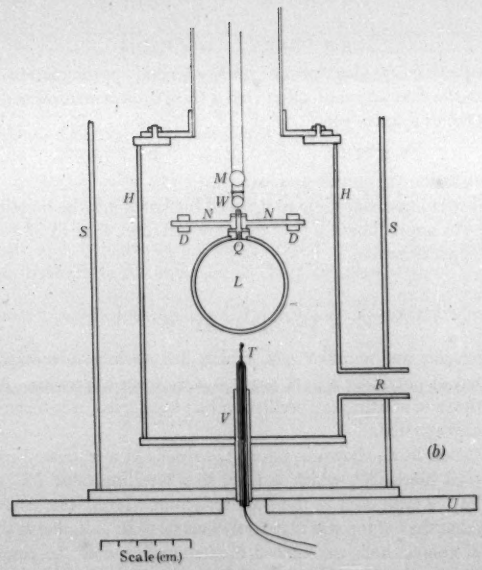


Figure 1.

a plug *C*, which fits tightly into it, they must be equidistant from the axis of the suspension head, and when the top of the head is accurately levelled the axis must be truly vertical. To aid in the levelling a table *KK* is provided.

A rotation of the head will impart a true rotation to the sphere if it is hanging with its centre of mass on the truly vertical axis of the conical head. To ensure this the bifilar suspension is made of a single wire, the loop of which carries a small wheel, *W*, provided with a fine circumferential groove, figure 2. The frame *TT* (seen from front and side in figure 2 *a* and *b*) which also carries the sphere, is provided with a horizontal bar just above the wheel, whose width is slightly less than

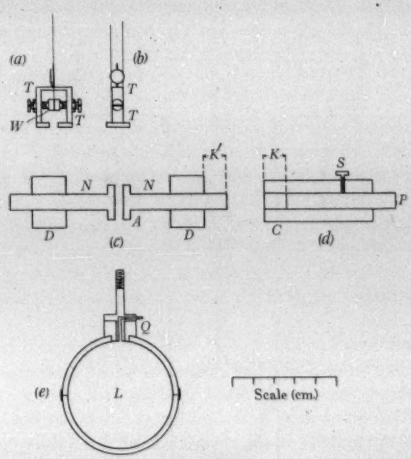


Figure 2.

the diameter of the groove. The two wires, therefore, just clear the sides of the bar, which are covered with a thin layer of sealing wax, except near the points where the wire passes. After the suspension is in position, and the centre of the mass of the whole suspended body has settled in the axis of the head, the wax is melted with a special electric heater, and fixes the suspension wires rigidly to the bar, without having to bear any weight. In this way any uncertainties of motion, which would occur if the sphere were suspended by the wheel, are eliminated.

The frame *TT* is fastened by nut and screw to the block *Q*, which is attached to the sphere *L* and also carries the inertia bar *NN*. The hole in *Q*, used during the filling, is closed by a plug. The whole suspension and sphere is in a vacuum-tight enclosure, as shown in figure 1. This consists of a glass tube *GG*, a metal box *HH*, surrounded by a water jacket and suitable windows, and a tombac bellows *EE*, connecting the brass plate holding the glass tube to the brass plate soldered to *BB*. This bellows was found convenient in avoiding any strain on the suspension head

or on the glass tube. Long metal screws, shown in the diagram, were used to prevent the bellows collapsing when the system was evacuated. The evacuation was carried out with a mercury vapour pump, suitably backed, and the vacuum produced was estimated at about 10^{-5} mm. of mercury, or less. The temperature was taken by the thermocouple *T*.

The arrangement shown in figures 1 and 2 is designed for the accurately ground sphere (see § 5), and was adopted for a limited range of temperature, in the neighbourhood of room temperature, only. Spheres blown on the end of tubes were also used, especially for higher temperatures. Such a sphere is shown in figure 3,

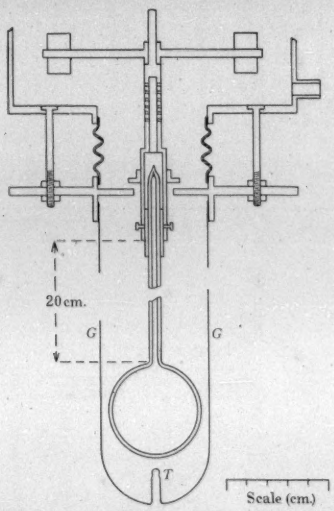


Figure 3.

with the inertia bar attached. The suspension arrangement was the same as that shown in figure 1. The sphere was surrounded by a glass tube *GG*, the depression *T* being designed to receive a thermocouple. The heating was done by means of an electric furnace surrounding the whole of the tube *GG* except the uppermost few inches, which were kept cool by a water jacket.

The amplitude was recorded photographically. A celluloid scale was mounted so as to form the arc of a circle of about 1 metre radius, and fixed so that the moving mirror lay at its centre, the path of the beam from the mirror to the scale being included in a light-tight box. A strip of photographic paper was then fastened to the far (graduated) side of the celluloid. With light of a suitable strength the extremities of the swing left a clear trace on the paper, on which the scale was also recorded, so that deformation of the paper during printing and drying did not

affect the accuracy of the results. From the photographic record the logarithmic decrement was calculated. Successive experiments at the same temperature gave differences in the decrement not exceeding 1 part in 2000.

The correction for external damping was made by taking the logarithmic decrement with the empty sphere. A swing of amplitude 20 cm. diminished by not more than 1 cm. in an hour. The correction varied from 0·5 to 0·8 per cent with the different spheres.

The expansion of the glass with temperature is so small over the range of 60° C. (coefficient of linear expansion of pyrex glass is 3×10^{-6} per deg. C.) that the correction for change of R with temperature is practically negligible, the extreme variation causing a change of about 0·1 per cent in the calculated value of η.

§ 4. THE DETERMINATION OF THE MOMENT OF INERTIA OF THE SUSPENDED SYSTEM

The moment of inertia of the suspended system must be accurately known, as the calculation of η involves the square of this quantity. There are two main difficulties: firstly to get standard inertia bars, of equal weight but different values of moment of inertia, which must be sufficiently true for the moments of inertia to be calculated with the required accuracy from their geometrical measurements; and, secondly, to avoid any change in the suspension wires, due to tension or other causes, when the inertia bars are interchanged. The second difficulty can be avoided by careful manipulation: to meet the first the following disposition was adopted.

The standard inertia pieces consist of a central rod and two thick discs, *DD*, figure 2*c*. To ensure uniformity in density, and true geometrical form, the rod and the weights are cut from a single large block of brass and carefully turned in the lathe. In the middle of the rod is left a block *A*, with a central hole through which the rod and the weights can be attached to the oscillating system. There is close sliding fit between the weights and the rod.

Measurement in an accurate gauge, kindly put at our disposal by the Engineering Department of University College, showed that the greatest variation in diameter in one disc was 1 part in 4000, while in the other it did not exceed 1 part in 20,000; the mean diameter of the two discs differed by 1 part in 5000. The thickness showed a like uniformity and the diameter of the central rod had as extreme values 0·4770 and 0·4775 cm. To adjust the distances of the weights from the centre of the rod a special gauge was made, shown at *CP*. This consisted of a cylinder *C* with an adjustable piston *P*, fixed in position by the screw *S*, figure 2*d*. The depth *K* of the cylindrical cavity having been carefully measured with a depth gauge reading to 0·01 mm., the gauge is then pushed over the rod, displacing the disc *D*. The distance K' is then accurately equal to *K*, the nature of the contacts made by the depth gauge being very similar to those made in the adjustment. It may be mentioned that a groove is cut along the rod of the gauge to give an outlet for the trapped air. Three different moments were used, and three different gauges were made and kept fixed, one for each adjustment.

I_1 The moment of inertia of the system is made up of a fixed part I_1 due to the
I_n sphere and inertia rod, and a variable part I_n, due to the movable discs in position n, which can be calculated.

We have $$T_n = 2\pi \sqrt{\frac{I_1 + I_n}{f}},$$

T_n where T_n is the time period corresponding to I_n.

The restoring couple f is independent of the moment of inertia, the load being the same in all cases. Any two values of n enable I_1, and hence the total moment of inertia actually used in the experiment to be found. Three different values were actually used giving two independent values of I_1. In this way the moment of inertia was found with an error of not more than 1 part in 2000, which means an error in η of not more than 1 part in 1000.

§ 5. THE SPHERES

Five spheres were used in all. The first was a glass sphere 5·088 cm. in diameter, made in two halves, the glass being about 3 mm. thick. This sphere had been prepared for another purpose, and was stated to be true to within 0·02 mm., or 1 part in 2500. A hole in the one hemisphere received the brass block carrying the inertia bar and mirror, which was cemented in, and the two halves were fastened together by means of a brass ring and cement.

The other spheres were selected from a number of spheres of pyrex glass blown at the end of a glass tube. The diameters in various directions were measured by immersing the sphere in a mixture of benzene and methyl alcohol, of the same refractive index as the glass, and observing with a reading microscope directly on the inner surface of the glass. A 1-per-cent difference in the refractive indices gives rise to a 1-per-cent error in the measurement, so that the method is not satisfactory from the point of view of absolute accuracy unless the mixture is very carefully prepared. Our method was to use an approximately correct mixture in a preliminary test, to estimate the departures from sphericity, and later to make up the mixture very carefully, and measure the diameter in the neighbourhood of the equator, for reasons to be given shortly. The spheres were in general slightly flattened at the poles, but the greatest difference of diameters with those used was 0·04 cm. on a diameter of 4 cm. or so, or about 1 per cent.

The absolute value of R was estimated by weighing the sphere full of water, which gives, of course, a mean value of R^3. It should be noted that 88 per cent of the volume of the sphere is contributed by a zone bounded by planes passing through the latitudes of $\pm 45°$.

As the viscous torque on the sphere varies as $\cos^3 \chi$, the slight flattening matters very little, since 88 per cent of the damping takes place over the zone for which $\chi = \pm 45°$. Table 1 gives the calculated percentage of the damping due to different zones extending to either side of the equator up to the angle specified. It will be seen that the 30° in the neighbourhood of the pole ($\chi = 60°$ to $\chi = 90°$) contributes only 2·5 per cent of the damping, the 20° only 1 per cent and the 10° only 0·05 per

cent, so that the exact shape of the sphere when the tube joins it is immaterial. The average value of R from $\chi = 0°$ to $\chi = 45°$ was found to agree, in all cases, to within 1 part in 4000, with the value obtained by weighing, which, as we have seen, lays stress on the zone in question, and was therefore adopted.

Table 1

Latitude	10°	20°	30°	40°	50°	60°	70°	80°	90°
Percentage of total damping	25·8	49·3	68·7	83·1	92·4	97·3	99·4	100	100

§6. RESULTS

With the object of testing the method the viscosity of water was measured over a temperature range of from 2·5 to 65·2°, the five different spheres being used and two suspensions. The results are shown in table 2 and figure 4, the smoothed

Table 2. Viscosity of water

Sphere	Temperature	η observed	η (I.C.T.)	Percentage difference	Probable error (%)
A	2·5	0·01657	0·01647	+0·6	0·3
	5·6	0·01479	0·01491	−0·8	
	13·2	0·01208	0·01200	+0·7	
	15·4	0·01130	0·01133	−0·3	
	22·4	0·00951	0·00952	−0·1	
B	12·7	0·01212	0·01216	−0·3	0·3
	25·0	0·00895	0·00895	0·0	
	31·3	0·00772	0·00778	−0·8	
	51·7	0·00529	0·00534	−1·0	
C	17·5	0·01061	0·01073	−1·1	(0·6)
	65·2	0·00439	0·00436	+0·7	
D	17·5	0·01076	0·01073	+0·3	(0·4)
	40·0	0·00660	0·00654	+0·9	
E	19·8	0·01015	0·01014	+0·1	(0·1)

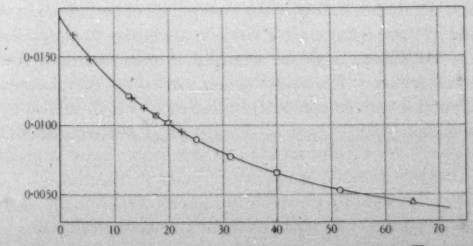


Figure 4. Sphere A, +; sphere B, ○; sphere C, △; sphere D, □; sphere E, ▱.

figures from the International Critical Tables (I.C.T.) being taken as standard. The probable errors for the determinations made with each sphere are given. The

worst value is for C, where there was a little uncertainty in the temperature. At the lower temperature a change of 1 per cent in the viscosity corresponds to an error of about 0·3° C., at the higher temperatures to an error of 0·8° C. No special precautions were taken to keep the temperature constant, and probably part of the error in the determination was due to fluctuations of temperature. It seems a fair conclusion for these experiments that, even with a blown glass sphere, not specially worked, the absolute value of the viscosity can be determined to within 0·5 per cent.

We can say, then, that the sphere method is probably capable of as great accuracy as any of the standard methods, and possesses the many advantages pointed out in the introduction. It is now being applied successfully to measure the viscosity of the molten alkali metals, and results will shortly be published.

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DISCUSSION

Dr Allan Ferguson. A relatively simple treatment of the problem of the oscillating sphere is to be found in Lamb's *Hydrodynamics*—a treatment which, so far as I remember, does not discuss the finer points of technique in the admirable manner adopted in these papers. It is subject, of course, to the βa condition, and the experimental conditions could be arranged to give results of the one or two-per-cent order of accuracy for fluids having viscosities of the order of that of water. I have found it convenient to determine moments of inertia by loading the sphere with an anchor ring.

532.137

ON THE DETERMINATION OF VISCOSITY BY THE OSCILLATION OF A VESSEL ENCLOSING A FLUID: PART 2

By Professor E. N. da C. ANDRADE, F.R.S.,

AND

LEONARD ROTHERHAM, M.Sc.

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ABSTRACT. A new method of carrying out the oscillating sphere method is described. The sphere containing the liquid carries a small permanent magnet, at the centre of a Helmholtz coil system. A condenser, discharged through the coils once in every complete swing, supplies the energy dissipated by the viscous forces, and so maintains a constant amplitude. Measurement of this amplitude, and of the potential of the condenser, enables comparative measurements of viscosity to be accurately made. The method has been checked by measuring the viscosity of hexane in terms of that of water. Absolute measurements are possible by the method, but have not been carried out.

§ 1. INTRODUCTION

In the method of measuring viscosity originated by Helmholtz and Piotrowski, to which part 1 of the paper is devoted, the energy of the oscillation is gradually dissipated by the non-conservative viscous forces, and the viscosity is determined by measuring the damping. It is possible, however, by supplying energy to the system at every oscillation to maintain a fixed amplitude, the amount of energy supplied to the system being then equal to that dissipated. The viscosity can then be calculated from the amplitude and the energy communicated.

The principle of the method to which this paper is devoted is as follows. To the sphere, suspended as before, is rigidly attached a short magnet of high coercivity. A pair of Helmholtz coils is arranged so that the magnet lies at the centre, with its axis normal to the axis of the coils when the sphere is at rest. By means of a beam of light reflected from a mirror attached to the sphere and a light sensitive relay a condenser of known capacity, at a known potential, is discharged through the coils when the oscillating sphere passes through its equilibrium position. An impulse proportional to the quantity of electricity passing through the coils is thus given to the suspended system within a time which is very short compared to the period, just as in a ballistic galvanometer through which a condenser is discharged. The amplitude of the swing will increase (or decrease) until the energy dissipated by the motion of the fluid is just equal to that supplied. As it is difficult

to set up mechanically an oscillation without pendulum swing, except by a very carefully constructed system (see part I) it is best to start with the sphere at rest, and let the condenser discharge work up the oscillation to its final amplitude.

§ 2. CALCULATION OF THE VISCOSITY

From equations (8) and (8*a*) of part I the moment of the viscous forces on the sphere is

$$P=\frac{8}{3}\pi\eta R^3\left(bR-2+\frac{1}{bR-1}\right)\frac{d\theta}{dt}=L\frac{d\theta}{dt}.$$

J The change of angular momentum J in time dt is therefore

$$dJ=L.d\theta,$$

or the change of momentum in one complete oscillation is

$$J=2L\,(\theta_1+\theta_2)=2L\theta_A,$$

$\theta_1, \theta_2, \theta_A$ where θ_1 and θ_2 are the extreme angular displacements, and θ_A is total angular displacement.

Taking the real part of L

$$J=2M\theta_A$$
$$=\frac{16}{3}\pi\eta R^3\left\{gR-2+\frac{gR-1}{(gR-1)^2+h^2R^2}\right\}\theta_A \qquad \text{.....(II, 1)}$$

Now in

$$g=\sqrt{\frac{\pi}{Tv}}.(1-\tfrac{1}{2}\Delta+\tfrac{1}{8}\Delta^2)$$
$$h=\sqrt{\frac{\pi}{Tv}}.(1+\tfrac{1}{2}\Delta+\tfrac{1}{8}\Delta^2)\Bigg\} \qquad \text{.....(I, 14),}$$

the value of Δ is small, being round about 0·02 or less in the present experiments. The term $\frac{1}{2}\Delta$ therefore represents a correction of about 1 per cent, while the term in Δ^2 is negligible. Hence a very rough value of the logarithmic decrement δ is sufficient: even an error of 10 per cent in δ makes an error of only about 0·1 per cent in J.

M The momentum supplied by the condenser discharge is MGQ where M is the
G moment of the magnet, G is the field produced at the centre of the coils by unit
Q, C current and Q is the quantity of electricity discharged through the coils. If C is
V, x the capacity of the condensers in farads, V the potential in volts, x the radius of
n the Helmholtz coils, of n turns, then

$$GQ=\frac{0{\cdot}899n}{x}CV.$$

If the moment of the magnet is measured, we can find a value for J in equation (II, 1), and hence an absolute value of the viscosity. In the above the damping due to residual gas in the evacuated space and imperfect elasticity of the suspension is neglected. It is, in fact, negligible in our experiments. Allowance can easily be made for it, if necessary, by finding, with the aid of a condenser of small capacity, the energy necessary to maintain the empty sphere in oscillation at a fixed amplitude.

It is, however, easier to calibrate the apparatus by using a liquid of known viscosity, preferably water. The method of proceeding is then as follows.

From equation (II, 1)

$$\eta\left\{gR-2+\frac{gR-1}{(gR-1)^2+h^2R^2}\right\}s=\frac{3MCL}{16\pi R^3}V$$
$$=KV \qquad \text{.....(II, 2),}$$

where L is the distance of the circular scale from the mirror at its centre, s is the total length of the arc of swing, and K is constant for a given sphere and a given capacity. The values of s, T and Δ having been found with a liquid of known η and ρ, and with a determined value of V, the constant K is known.* *L, s K*

Using the same sphere and capacity, but, if convenient, a different V, we find s, T and δ.

Since $g=\sqrt{(\pi/Tv)}$ approximately, while

$$\frac{gR-1}{(gR-1)^2+h^2R^2}=\frac{1}{2gR},$$

approximately, and is small (about 0·05 in these experiments) and can be neglected in comparison with $gR-2$ (about 10), we can write

$$\eta\left(\sqrt{\frac{\pi\rho}{T}}\cdot\frac{1}{\sqrt{\eta}}-2\right)s=KV \qquad \text{q.p.} \qquad \text{.....(II, 3),}$$

which, using our value of K, gives us a quadratic to find a first approximation for η. With this value of η we find an approximate value for $gR-1/\{(gR-1)^2+h^2R^2\}$ and, taking account this time of the $\frac{1}{2}\Delta$ term in g, solve the quadratic given by equation (II, 3) for η. If necessary a third approximation can be made.

As an example of the rapidity of convergence, using an experiment on water at 0°, with standard value $\eta=0{\cdot}01797$, to find K, equation (II, 3) gives, for an experiment on water at 25·0° C.,

$$\eta=0{\cdot}00907,$$

as a first approximation, while the second approximation is

$$\eta=0{\cdot}00902 \quad (0{\cdot}009019).$$

A third approximation is unnecessary: it gives 0·009016. The standard value is 0·00895.

§ 3. EXPERIMENTAL ARRANGEMENT

The sphere used was the accurately worked one, made in two halves cemented together, described in part 1. It was suspended by a bifilar arrangement from a plate *BB*, figure 1, supported by a massive beam, the lower end of the suspension being attached to a brass piece carrying the magnet *P* and two mirrors inclined at an angle to one another, one to reflect the beam operating the selenium relay, and the other to register the amplitude of the oscillations in the ordinary way. This

* The capacity C can, of course, be varied if desired, $K'CV$ then taking the place of KV, and K' being determined.

brass piece was rigidly fastened to a glass rod, some 20 cm. long, carrying the sphere at its lower end. The method of attachment of the suspension ensured that the centre of mass of the sphere lay in the line midway between the two vertical and parallel suspension wires.*

The whole suspended system was surrounded by a vacuum-tight enclosure attached to the plate *BB*. It consisted of a tombac bellows *D*, to allow flexibility during adjustment; a glass tube *HH*, about 82 cm. long; and a brass tube system,

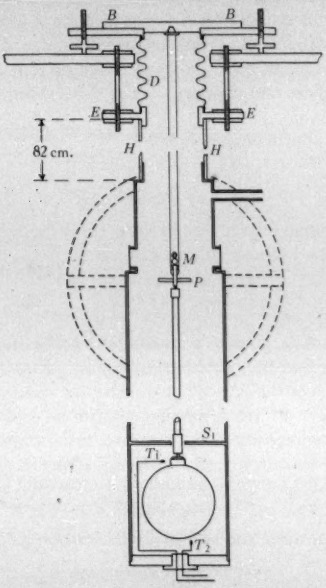

Figure 1.

provided with suitable windows to which the Helmholtz coils were rigidly attached. When the necessary adjustments had been made the plate *EE* was fixed by the screws shown, to avoid collapse of the bellows on evacuation.

To discharge the condenser automatically through the coils at the moment when the sphere passed through its equilibrium position a selenium cell with relay was employed. The usual simple device, by which the passage of the light beam across the cell operates a relay, is not suitable in the present instance, since there are two passages per complete oscillation which would produce identical results, and so lead to an impulsive force of one sign for the direct passage, and of the opposite sign for the reverse passage, which cancel out.

* See part 1, p. 255 and figure 1.

An optical arrangement was therefore used by which the cell is shielded from the light during one half of the complete oscillation, and illuminated during the other half, a suitable bridge arrangement ensuring that the condenser was charged when the cell was in darkness, and discharged when it was first illuminated. Light from a slit S is concentrated by the lens L on the plane mirror at M, and comes to a focus at F in the plane of the screen CD, being just at D when the mirror is in the equilibrium position (figure 2). A large plane-convex condensing lens BB is arranged with its plane face against the screen CD, and the selenium cell G is placed where BB forms an image of the surface of M. The large condensing lens does not, of course, give a sharp image but is good enough to ensure that sufficient light falls upon the cell for all positions that F actually takes up on the clear half of the lens.

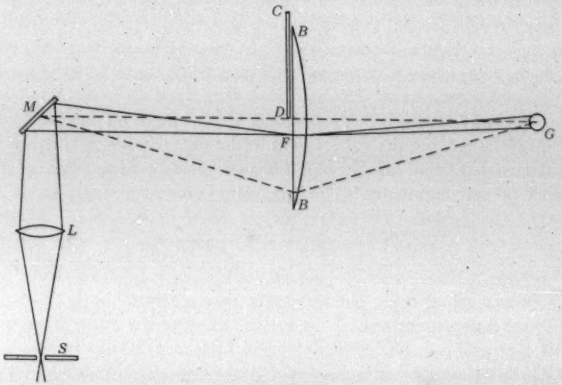

Figure 2.

In this way, instead of having two identical dark-light-dark passages per complete oscillation, we have one dark-light passage and one light-dark passage, which produce the required results. A separate mirror is used to record the amplitude.

Bright tin radiation shields, of which the lower one, S_1, is shown, helped to keep the temperature uniform in the enclosure. The temperature was recorded by two copper-constantan thermocouples T_1, T_2, one just above the other just below the sphere. They gave the same reading within 0·1° C. or less. The brass enclosure surrounding the sphere was jacketed with water kept at a thermostatically controlled constant temperature, or with water containing melting ice.

The pressure inside the enclosure was maintained at about 0·001 mm. of mercury or lower by means of a mercury vapour pump with the usual backing. The air damping appeared to be negligible. However, as was pointed out in § 2, the exact value of the (small) external damping is not necessary, as the whole damping appears only as a small correction in the final result.

§ 4. EXPERIMENTAL TEST OF METHOD

The method has not been used to find an absolute value of the viscosity, which demands an accurate measurement of the magnetic moment and a careful consideration of the field due to the coils, but only for comparative measurements. The apparatus can be easily calibrated with a suitable known liquid. In the present case we have used water, and carried out the following tests: (1) We have found two values of K, as described in § 2, by using water at two different temperatures. The two values agree well. (2) Using the value of K so derived we have found the viscosity of hexane, which is much less than that of water, at two different temperatures, and compared them with the standard values.

The two temperatures selected for water were 0·0° C. and 25·0° C. Taking the values of η as being respectively 0·01797 and 0·00895, and substituting the appropriate values in equation (II, 2) we find $K=0{\cdot}04661$ and 0·04669 respectively. As an example the actual figures for water at 0·0° C. were $\delta=0{\cdot}150$, $s=38{\cdot}084$ cm. (mean value for 30 swings, the extreme values being 38·06 and 38·16), $T=9{\cdot}014$ sec., $V=133{\cdot}8$ V., $R=2{\cdot}544$ cm.

Using the mean value of $K=0{\cdot}04665$, experiments on hexane yielded the following values, η being the value found in the experiments, and η_s the standard value, extrapolated from Thorpe and Rodger's value, with m taken as 1·1 in the Hagenbach-Couette correction.* The agreement is disconcertingly good.

Temperature (°C.)	η	η_s
0	0·003956	0·003965
21·9	0·003135	0·003137

§ 5. ADVANTAGES OF THE METHOD

The method possesses, of course, the advantages of any method in which the liquid is enclosed in a sealed vessel throughout the experiment, to which allusion has been made in part 1. As against the method there described it has certain additional merits. (1) It is in some respects easier to set up the apparatus in the first case, as the carefully worked suspension head is eliminated. (2) The actual readings to be made are much simpler. Instead of the photographic registration of a long series of swings, which is necessary if the logarithmic decrement is to be found accurately, there is only the (constant) amplitude of swing to be noted. (3) The calculation is shorter. (4) The correction for the inherent damping of the system due to the suspension wires and the residual air is very simply made if it is necessary to take it into account.

As regards accuracy, there is probably little to choose between the two methods, although, if anything, the second method is perhaps capable of the greater refinement.

§ 6. ACKNOWLEDGMENT

We are much indebted to Mr Y. S. Chiong for help with the calculations.

* See Andrade, *Phil. mag.* **17**, 708 (1934).

538.632

A METHOD OF INVESTIGATING THE HALL EFFECT

By H. STAFFORD HATFIELD, Ph.D.

Received May 23, 1935. *Read December* 20, 1935

ABSTRACT. A cylindrical coil of thin metal strip of width equal to the length of the coil is connected to a galvanometer and set between the poles of a magnet rotating about the axis of the coil, the field being at right angles to the latter direction; or a stationary three-pole magnet fed with three-phase current may be used. The galvanometer indicates a steady direct e.m.f. due to the sum of two Hall e.m.fs. per turn of the coil, resulting from the action of the field upon the currents induced in the coil by the rotation of the field. The e.m.fs. are much larger than those obtainable by ordinary methods, and there are no thermoelectric or other disturbing effects. An approximate formula is derived, and is shown to agree roughly in the case of seven metals with data taken from tables. It is suggested that the method might be of use for comparative work at extreme conditions.

§ 1. OUTLINE OF THE METHOD

The usual method for measuring the Hall effect consists in placing between the poles of an electromagnet a strip of the metal under examination and passing through it a primary current as large as possible and usually direct. At two points at opposite ends of an equipotential line on the strip electrodes connected to a sensitive galvanometer are applied, so that no current passes through them when the magnet is unexcited and the electrodes are truly placed. When the magnet is excited, the galvanometer indicates the presence at the electrodes of an e.m.f. E_H given by E_H

$$E_H = \frac{RHi}{d},$$

where H is the field, i the primary current, d the thickness of the strip in the direction of the magnetic field, and R the Hall coefficient. For most metals R in absolute units is of the order of 10^{-3} and for the magnetic metals of 10^{-2}, while for antimony it is 10^{-1}, for bismuth from 1 to 10, and for tellurium 500. Possible values of i are limited by the specific resistances of the metals, which, very roughly speaking, follow the Hall coefficient in magnitude. Hence the larger the R to be measured, the smaller is the current which can be used for measuring it. The practical outcome is that Hall coefficients are determined by the measurement of a very few microvolts, and usually on thin specimens the thickness of which enters directly into the formula. The small transverse e.m.f. is measured in the presence of the large primary current and its corresponding potential fall. H, i, d R

The obvious disadvantages attendant on this arrangement are mitigated to some extent by the use of alternating primary current and an alternating field, but the smallness of the measured e.m.f. remains, and no advantageous method of increasing it by summation of a number of sources has yet been devised.

The purpose of the present paper is to describe a method of exhibiting the Hall effect based upon the principle of generating the primary current by the inductive action of a rotating magnetic field upon a cylindrical sheet of the metal set coaxially with the axis of rotation of the field. The Hall effect then arises from the action of the same magnetic field upon the currents so induced. This method has the advantage of dispensing altogether with delicately adjusted Hall electrodes, and the further advantage, if a cylindrical coil of sheet metal of many turns is used, of allowing a large number of Hall e.m.fs. to act in series. In these experiments,

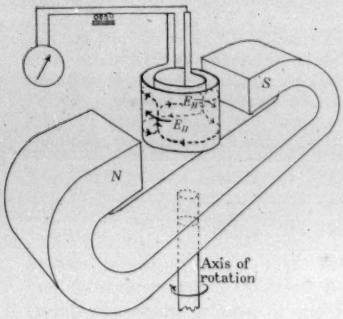

Figure 1.

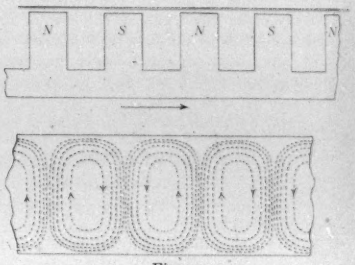

Figure 2.

Figure 1. Generation of Hall e.m.f. E_H in a strip metal coil exposed to the field of a rotating magnet, the Hall coefficient being positive.

Figure 2. Diagram of current eddies in strip exposed to field of moving magnetic poles.

metals with a low coefficient were made to deliver a Hall e.m.f. exceeding 100 μV. in fields of only 3000 G., and it would be easy to multiply this many times.

The general principle of the method will be clear from figure 1. A long strip of the metal under investigation is wound into a close spiral and exposed to a magnetic field at right angles to the axis of the spiral and rotating about it. A system of induced currents is set up in the spiral as indicated by the dotted lines in the figure, and the action of the field on these currents generates Hall e.m.fs. The Hall e.m.f. generated in each current-path parallel to the axis is in the same sense with reference to the axis, since the directions of both current and field are opposite on opposite sides of the spiral. The Hall e.m.fs. therefore add up in each turn, and from turn to turn. Figure 2 makes this clearer by exhibiting the strip as unrolled and exposed to the fields of a series of alternate magnetic poles moving beneath it in the direction of its length, the induced current eddies being suggested by the dotted lines.

We shall in the next section describe the results of measurements of the e.m.f. under different conditions and in different metals, and give the experimental evidence that this e.m.f. is connected simply with the Hall effect, reserving for § 3 a discussion of the system of induced currents, and the theoretical reasoning which supports the above conclusion.

§ 2. EXPERIMENTAL DETAILS

We will first describe the experiments carried out with copper sheet 0·05 mm. thick. A strip of this, 19·6 mm. wide, was wound upon a brass rod 3 mm. in diameter to form a coil of 16 turns, which were insulated from one another by paper tape. The magnet used was a specially designed magnet with an iron circuit, shaped as a rectangle with a central crossbar (i.e. two rectangles having one side in common), and set with the pole axis horizontal upon a turntable having a vertical axis. This form of magnet is especially suitable for the purpose, since the centre of gravity is low. The maximum attainable field was 7000 G. in a space 1 cm. long and 2·5 cm. in diameter, the copper coil being set in the centre of this with its axis vertical. The maximum safe speed of rotation was 600 r.p.m. An ordinary counter was used to measure it.

The strip coil was connected through a 20-Henry wireless choke to a galvanometer of 100 ohms resistance, the total resistance in circuit being about 300 ohms. The sensitivity of the arrangement was found to be 15·1 μV./cm. on the scale. The choke is necessary, since the inevitable departure from symmetry of the arrangement leads to the appearance at the terminals of the coil of an alternating e.m.f. It is clear that a much more powerful magnet, and higher speeds of rotation, could be used if the coil instead of the magnet were rotated, but this would involve slipping contacts in the galvanometer circuit.

Measurements were made of the deflection of the galvanometer for various speeds of rotation and various values of the magnetic field. If the deflections are in fact due to the Hall effect and therefore dependent upon the product of the magnitude of the induced currents and the field to which they are exposed, then, in accordance with § 3, we should expect the galvanometer deflections to increase linearly with the speed of rotation but according to the square of the magnetic field. Figure 3 shows the relation between observed microvolts and speed of rotation, and it will be seen that within the accuracy of the observations the dependence is approximately linear. This proves no more than that the effect is due in some way to induced currents.

Figure 4 shows the dependence of the direct e.m.f. upon the magnetic field-strength, and there is good evidence for a linear variation with H^2. This suggests very strongly that we are here concerned with an action of the magnetic field upon the induced currents, which themselves depend upon field-strength.

The final proof of the Hall origin of the effect was then obtained by performing experiments with different metals. These were carried out by means of a specially constructed three-pole magnet fed with three-phase 50-cycle current from the mains. The pole-gap was cylindrical (like the pole-tunnel of an induction motor)

being 12 mm. in diameter and 20 mm. long. The pole-surfaces occupied about half the periphery. A field of 3000 G. could be maintained continuously, and 4100 could be obtained on overload. The average value of the stray field over a distance at either end along the axis of the pole-tunnel and equal to its length was about one-half of the above.

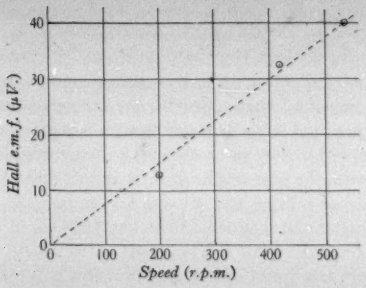

Figure 3. Relation between Hall e.m.f. and speed of rotation of field.

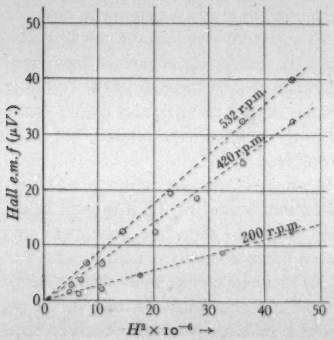

Figure 4. Relation between Hall e.m.f. and square of strength of rotating magnetic field.

Experiments were first made with the 0·05-mm. copper sheet to determine the effect of the width of the strip upon the e.m.f. developed. It will be seen from figure 5 that there is an optimum value for the width, as might be expected. When it much exceeds the axial length of the field space, the Hall current can take a short-circuit path along its edges. On the other hand, as the width of the strip is diminished the induced e.m.f. is diminished in like proportion, while the ohmic resistance to the induced currents diminishes much more slowly, and finally increases. The general shape of the curve is thus accounted for. For the experiments which follow, a strip width of 25 mm. was chosen.

The table shows the observed values in absolute units of the e.m.fs. generated in coils of this width, but of various lengths and thicknesses of strip, in the three-phase field of 3000 G., as compared with the Hall coefficients and specific resistances of the metals taken from tables.*

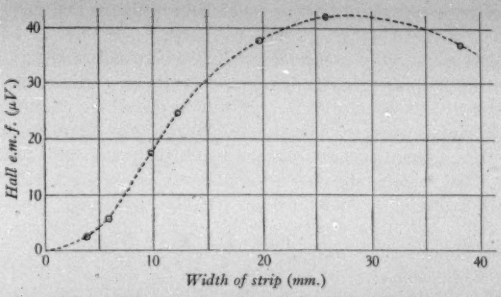

Figure 5. Hall e.m.f. delivered by coils of copper strip differing only in width.

Table

Metal	E.m.f. observed (absolute e.m.u.) E_H	Hall coefficient (absolute e.m.u.) R	Specific resistance (absolute e.m.u.) σ	Length (cm.) L	Thickness (cm.)	Turns n	$\frac{4E_H \sigma n}{RL^2} \times 10^{-8}$
Aluminium	− 1,350	−0·0004	2,820	55	0·0025	23	2·9
Copper	− 4,077	−0·0005	1,720	60	0·0078	20	3·1
Lead	+ca. 50	+0·0001	20,630	35·3	0·02	14	4·7
Nickel	+33,900	+0·012	7,240	87·5	0·0045	34	3·6
Silver	−14,900	−0·0008	1,620	122	0·0025	48	3·9
Zinc	+ 1,440	+0·001	5,920	62	0·0097	23	2·0
Tin	0	−0·00002	11,400	100	0·0025	45	—

The signs attached to E_H in the second column are chosen arbitrarily so that a metal having a positive Hall coefficient should, if the scheme of figure 1 is correct, give rise to a positive E_H, and *vice versa*. A positive Hall coefficient gives rise to a current through the coil and galvanometer flowing through the former in the same conventional direction as the rotation of the field. The simple electron theory of the Hall effect predicts a negative coefficient, and in this case the *electron* current is in the same direction as the rotation of the field.

It will be shown in the next section that if the e.m.f. is due only to the Hall effect, the figures in the last column should be constant and of the order $4{\cdot}5 \times 10^8$. In view of the very rough character of the calculation, the resulting agreement is very satisfactory. It may be noted in passing that Sommerfeld and Frank[1] say that "the Hall effect can be relied upon on the average with a precision of some 30 per cent".

* R from Campbell, *Galvanomagnetic and Thermomagnetic Effects* (London, 1923) and σ from Childs, *Physical Constants* (London, 1934).

The conspicuous absence of bismuth from the table is, of course, due to the fact that the construction of strip coils of many turns would be difficult on account of its brittleness. Taking a value $3{\cdot}0 \times 10^{8}$ for the last column, R for bismuth as 6·0, σ as 119,000, and $L = 2n$, we calculate E_H/n to be 150 μV. *per turn*. A bismuth coil should thus be capable of yielding much larger voltages than those measured above.

The absence of the effect in mercury is well known, and an effort was made to determine it by the present method, which presents great advantages for liquid metals in view of the avoidance of the well-known disturbing effects arising from the flow of the metal under the electrodynamic forces. A mercury coil was made as follows. A strip of paper 35 mm. wide and two strips 5 mm. wide were saturated with paraffin wax. A glass tube of external diameter 4 mm. was closed at one end, and a hole was blown in the side of it 1 cm. from the closed end. The wide and the two narrow strips were then wound together on the tube at the closed end, the narrow strips being set along each end of the wide strip, so as to space apart the convolutions of the wide strip by the thickness of the narrow strip. The coil was then thrust into a test tube at the bottom of which was a little molten wax, and some wax was also melted over the coil at the upper end by means of a hot glass rod, care being taken to leave a space at one point between the coil and the glass. Finally, mercury was poured down the centre tube; it filled the space between the convolutions of the paper, so forming a continuous coil of the size and shape of the strip coils used in the other experiments. It had 20 turns. It was thus comparable with the copper coil, which gave an e.m.f. of about 40 μV.; if its Hall coefficient were the same as that of copper, it might be expected to give about 1·8 μV., since its specific resistance is much higher. Not the slightest effect on the galvanometer could be observed, though less than 0·5 μV. could certainly have been detected. The experiment is only valuable as an illustration of the ease with which spurious effects can be eliminated by the present method.

The summation of the e.m.f. along the strip was confirmed by providing a copper strip coil 60 cm. long with tappings every 10 cm. The coil had 20 turns, but the tappings were of course not equally distributed as regards these, since the internal diameter of the coil was 3 mm. and its external diameter was 10 mm. Nevertheless, the e.m.f. from tapping to tapping was almost identical within the limits of error of the readings. The reason for this is seen in the light of the discussion given in the next section.

The induced currents are considerable, and an estimate of their magnitude can be derived from the following experiment on their heating effect. The silver coil referred to in the table was placed in the three-phase field, and its rise of temperature was determined by measuring its increase in ohmic resistance; it was found to have increased by 19° in 3 minutes. Now, for a metal of specific resistance σ, specific heat C, and density δ, the rate of increase in temperature due to current density u is, when losses are neglected, given by the equation

$$\frac{dT}{dt} = \frac{u^2\sigma}{C\delta}.$$

Taking $\sigma = 1{\cdot}64 \times 10^{-6}$, $C = 0{\cdot}056 \times 4{\cdot}2 \times 10^{7}$, and $\delta = 10{\cdot}5$ we find for u the value 398 A./cm.²

This is the r.-m.-s. value for the whole strip. The currents do not occupy more than half the area of the strip, so we may safely double the above value, and make it say 800 A./cm.² The strip being 0·0025 cm. thick, and the current paths on the average about 1 cm. wide, the currents must be of the order of 2 A. From this experiment a further important result will be obtained in the next section.

§ 3. DISCUSSION OF RESULTS

The following discussion makes no claim to completeness or exactness. It is justified by the fact that with the simple formulae obtained the experimental results can be calculated almost within the limits of error of the present experiments, and of the physical constants used.

The case resembles that of the well-known squirrel-cage alternating-current induction motor with its armature held stationary; there, however, the induced currents are forced into well-defined paths by the construction of the rotor. In the present case a calculation of the distribution of the induced current obviously presents great difficulties; even if an approximate solution were found for complete turns, the discontinuities introduced at the two ends of the coil would introduce further difficulties.

As in the squirrel-cage motor, the induced currents must lag behind the inducing field by an amount given by $\cos\phi = W/\sqrt{(W^2 + 4\pi^2 f^2 L^2)}$, where W typifies the resistance of the current path, L its inductance, and f the frequency. In the present arrangement, a further complication is introduced by the fact that the inner turns are shielded by the outer turns, and hence the phase angle may differ from turn to turn. W L, f

It will be seen that, in general, any calculation which neglects the phase angle will give too large a result, since the Hall intensity affecting the galvanometer is directed at right angles to the field, and this is directed at an angle ϕ to the strip at the point where the induced current is flowing. ϕ

However, leaving that point out of consideration for the moment, we can easily find from dimensional arguments that the Hall e.m.f. E_H will be given by an expression

$$E_H = RH^2 \Phi \left(\frac{f}{\sigma} L^2\right) \qquad \text{.....(1),} \qquad \Phi$$

where L^2 denotes some homogeneous expression of the second degree of the dimensions of the spiral coil. In order to obtain further details about the form of the function Φ, and information as to the manner in which the various dimensions of the coil enter into L^2, we suggest the following considerations based on approximation to the actual conditions.

Consider a metal foil in the y, z plane, exposed to a magnetic field H_x in the x direction. If H_x varies, we have as a first approximation in any one spot H_x

$$\sigma\left(\frac{u_z}{y} - \frac{u_y}{z}\right) = -\frac{dH_x}{dt} \qquad \text{.....(2),}$$

σ, u_z, u_y where σ is the specific resistance, u_z current density in the z direction, and u_y that in the y direction.

I The Hall intensity I measured on the galvanometer is due to the component in the direction y, and in general

$$I_y = R\,[\bar{u}_z . \bar{H}_x] \qquad \text{.....(3).}$$

There is also an I_z equal to $R\,[\bar{u}_y . \bar{H}_x]$, but this does not affect the galvanometer.

On the centre line of the strip, and at a point near to each pole, u_y will be small but u_z large. Here will arise the main external Hall e.m.f. Very approximately we may write

$$u_z \sim \frac{1}{\sigma} \int \frac{dH_x}{dt}\, dy \qquad \text{.....(4).}$$

The time factor can only introduce the frequency of rotation f into the numerator, hence u_z will depend mainly upon a quantity $\int H_x dy$, that is to say, on the magnetic field integrated in a horizontal direction perpendicular to H.

In order to obtain the Hall e.m.f. from the Hall intensity, we have to perform an integration right along the spiral length; thus by inserting equation (4) in equation (3) we obtain

$$\text{e.m.f.} = R \int^{\text{Whole length}} Iy\, dy$$

$$= \frac{Rf}{\sigma} \int^{\text{Whole length of foil}} H \int^{\text{Breadth of field}} H\, dy\, dy \qquad \text{.....(5).}$$

As a very rough approximation, we may obtain the order of magnitude of these integrals by equating them to

$$H^2 \times (\text{total length of foil exposed to magnetic field}) \times (\text{average length exposed to field in any half turn}).$$

Each of these lengths may be taken very approximately as one-half of the actual length of the strip.

Finally, we get for the n turns of the coil, made of strip having an actual length L,

$$E_H = KfH^2 \frac{RL^2}{4n\sigma} \qquad \text{.....(6),}$$

K where K is a constant of the order of unity.

fH^2 was constant throughout the experiments, hence $4E_H n\sigma / RL^2$ should be constant. It will be seen from the table that this was remarkably near to being the case. Still more surprising, in view of the very rough derivation of the formula, is the close approximation of these values to fH^2, which was $4{\cdot}5 \times 10^8$. We even see that the actual values are on the average somewhat smaller than this, as is to be expected in view of the neglect of the phase angle.

As a further argument in support of the view we have put forward, we may now consider the experiment, described in the last section, in which the rate of rise of temperature of the silver coil was measured. The Hall intensity is given by $R\,[\bar{u} . \bar{H}]$, where u is the current density at a point where the field is H. In the preceding section, the average value of u was obtained from the relation $u^2 = C\delta dT / \sigma dt$.

Since the final potential-difference is due to the intensity integrated along the length of the strip, we may write

$$E_H = RHL\frac{\int \delta dT}{\sigma dt} \qquad \text{.....(7),}$$

where L is the actual length of the strip, since it was all heated, and the value of u was obtained from its rise in temperature. Using the values given in the table, and the rise of temperature as given in the preceding section, we find for E_H the value 150μV.; the observed value was 149μV. The close agreement is, of course, quite fortuitous, but it clearly proves that the above treatment of the phenomenon cannot be very far wrong.

§ 4. CONCLUSION

The foregoing experiments and discussion appear to establish the fact that the e.m.f. measured is entirely due to the Hall effect. The effect is comparatively large and hence easy to measure with accuracy, and no spurious or disturbing effects are found to occur, the readings of the galvanometer being in all cases extremely steady and reproducible. While the absolute values as derived from the formulae given are obviously uncertain in view of the very rough derivation of these formulae, it would appear that comparative measurements would yield results of considerable accuracy, especially if the specimens used were alike in all dimensions. The discussion suggests that it might be best to keep f/σ and not f constant, in which case the relative values of R should be independent of phase relations. Since the e.m.f. measured is the sum of a large number of single e.m.fs., the unavoidable variations in the thickness of the specimen tend to average out. The thickness enters into the formula in the value of σ, but its determination on the actual specimen is more satisfactory than in the usual method, since a much longer strip is used.

If a suitable container could be constructed of rigid and permanent insulating material capable of standing elevated temperatures, it is probable that the method would present great advantages for liquid metals. At low temperatures also it should be advantageous when measurements on single crystals are not required.

§ 5. ACKNOWLEDGMENTS

This work was carried out in the Physics Department of University College, London, under a Fellowship grant from the Leverhulme Trustees, to whom I wish to express my thanks. I am also grateful to Prof. E. N. da C. Andrade for the kind and helpful interest which he has taken in the work, and the facilities which he has placed at my disposal.

Note added January 4, 1936

When this paper was read, I pointed out that the observed direct current produced by the rotation of the magnet, though readily explicable by combining the law of electromagnetic induction with the known facts of the Hall effect, seemed to conflict with the usual conception of electromagnetic induction. If a fixed homogeneous

metallic circuit is exposed to a cyclically varying magnetic field, the constants of the circuit remaining unchanged throughout the cycle of the field, the flow of electricity resulting from increase in the flux linked with the circuit should be equal and opposite to that resulting from decrease, and the generation of a balance of unidirectional current should be impossible. This argument was often used against the innumerable attempts by inventors to effect such a result in the early days of dynamo development.

A further remark may be of interest. If we replace the strip coil of figure 1 by a simple hollow cylinder, we must say that the induced currents flow in a direction not at right angles to the field and to its motion, but slightly inclined one way or the other. This must also be true in the homopolar ("unipolar") dynamo, where a copper tube rotates in a concentric pole gap like that of a loud-speaker magnet. If instead of rotating the tube, we apply an external source of e.m.f. to its ends, the fall of potential for a given current will be increased when the magnet is excited, for a Hall current will flow peripherally around the tube. As Bridgman showed[2] the energy of a Hall current is derived from an increase in potential-fall in the primary circuit. Making use of this, it is easy to show that the resistance ρ of the part of the tube exposed to the field will apparently increase by an amount $\Delta\rho$ given by

$$\frac{\Delta\rho}{\rho}=\frac{R^2H^2}{\sigma^2}.$$

In this case the direction of primary current-flow is undoubtedly changed from axial to spiral, and is presumably inclined to the acting e.m.f. The primary current is forced by the field to take a longer path of increased resistance, and the Hall current is simply the peripheral component of the primary current. This picture of the Hall effect seems to me physically simpler and more fundamental than the usual conception, concerning which much confusion has in fact arisen, as Campbell points out. However, ordinary magneto-resistance introduces a complication, for it would lead in most cases to an increase greater than that due to the Hall effect, as the following table shows. The data for R and σ are those given in the paper, and the magneto-resistance coefficients C (of H^2) are taken from *International Critical Tables*:

Metal	R^2/σ^2	C
Copper	$8{\cdot}5\times10^{-14}$	$2{\cdot}7\times10^{-13}$
Lead	$2{\cdot}35\times10^{-17}$	$5{\cdot}2\times10^{-14}$
Silver	$2{\cdot}45\times10^{-13}$	$2{\cdot}5\times10^{-13}$
		$3{\cdot}7\times10^{-13}$
Zinc	$2{\cdot}9\times10^{-14}$	$8{\cdot}5\times10^{-13}$
		$1{\cdot}4\times10^{-12}$
Tin	$3{\cdot}05\times10^{-18}$	$2{\cdot}3\times10^{-13}$

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535·332:546.15

REGULARITIES IN THE SPECTRUM OF TREBLY IONIZED IODINE

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ABSTRACT. The spectrum of a condensed discharge through iodine has been photographed in the region λ 6000 to λ 1900 under varying conditions of excitation, and about 70 lines have been ascribed to trebly ionized iodine. Among these more than 30 lines have been classified; assignments for the levels have been suggested on the analogy of the other isoelectronic spectra, Te III, Sb II and Sn I.

§ 1. INTRODUCTION

After the analysis of Te III carried out in this laboratory[1], an investigation of the spectrum of trebly ionized iodine I IV was undertaken. The spark spectrum of iodine has been studied by Wood and Kimura[2], Konen[3], Exner and Haschek[4], Asagoe[5], L. and E. Bloch[6], and Kerris[7], but an analysis of the spectra due to the higher ionized stages of the atom has not been attempted by any one of the above investigators. Recently, Lacroute[8] studied the Zeeman effects in some low-stage iodine lines and published an analysis of I II. Our knowledge of the structure of Te III made possible the prediction of the probable values of the intervals and the positions of the characteristic lines in the spectrum, and facilitated the discovery of several regularities among the lines due to I IV. It is the purpose of this paper to report these regularities.

§ 2. EXPERIMENTAL

In the experiments of L. and E. Bloch, the spectrum of I IV appears to have been excited very feebly, the lines recorded by them being faint. A reinvestigation was made by the writer, in which the spectrum was excited much more intensely. The source used was a highly condensed discharge through a capillary tube. Pure iodine, or in some cases iodide of copper supplied by Kahlbaum, was placed in a side bulb of the discharge tube. After the tube had been worked for some time by periodical gentle heating of the bulb, the heat of the discharge was sufficient to keep the capillary filled with iodine vapour. The discharge was run by a ½-kW. transformer and condensed by a capacity of about 0·05μF. An auxiliary spark gap and a self-inductance used in series with the discharge served, as usual, to alter the degree of excitation. While the discharge was running, a deposit of iodine was formed on the quartz window of the discharge tube, which necessitated frequent cleaning and refixing of the window during the experiment. The exposures extended from two to three hours. Ilford special rapid plates were employed, and for the ultra-violet between λ 2400 and λ 1900 the plates were sensitized by paraffin oil. As, however,

these sensitized plates were found unsuitable for measurement, Schumann plates prepared by the writer after the manner described by Schumann[9] were used. The instruments employed were a Hilger quartz spectrograph E 315 for the region λ 5000 to λ 1900, and a glass Littrow spectrograph for the entire visible region.

§ 3. ANALYSIS

The spectrum of I IV resembles that of Te III, and a brief statement of the important terms predicted by Hund's theory is presented in table 1.

Table 1

Term prefix	Terms
$6s$	^3P; ^1P.
$5d$	^3F, ^3D, ^3P; ^1F, ^1D, ^1P.
$6p$	^3D, ^3P, ^3S; ^1D, ^1P, ^1S.

The number of lines attributable to I IV are comparatively few, so that, although the characteristic intervals are large, the selection of multiplets was not found difficult. By extrapolation from the known values of the interval $6s\ ^3P_1$–$6s\ ^3P_2$ in the isoelectronic spectra Sn I, Sb II, Te III, the probable value of the corresponding interval in I IV could be arrived at. The regular diminution in the values of the screening constant with increasing nuclear charge in these spectra is shown in table 2. The value finally obtained in I IV is also included for comparison.

Table 2. The law of screening constants

Spectrum	Interval $6s\ ^3P_1$–$6s\ ^3P_2$	Screening constant	Difference
Sn I	3715	27·1	2·64
Sb II	5739	24·46	1·94
Te III	7698	22·52	0·72
I IV	8532	21·8	

The approximate position of the combination $6s\ ^3P_2$–$6p\ ^3P_2$ could be predicted from the sequence presented in table 3. A search for recurring pairs in the region below λ 4000 revealed three pairs having the fundamental difference 8532 cm.$^{-1}$

Table 3. The law of irregular doublets

Spectrum	$6s\ ^3P_2$–$6p\ ^3P_2$	Difference
Sn I	8605	7838
Sb II	16448	7805
Te III	24248	6862
I IV	31110	

When the combination $6s\ ^3P_2$–$6p\ ^3P_2$ was thus identified it was easy to extend the analysis to include the other $6p$ term-combinations.

The results are presented in multiplet form in table 4, which includes regularities among only those lines which could be confidently ascribed by the writer to I IV; lines of doubtful assignment are provisionally excluded. An analysis of the lines of I III, which is also being carried out by the writer, will decide their classi-

Table 4. Terms and multiplets of I IV

Odd terms \ Even terms				*a* $6p\ ^3D_1$ 158739·4	*b* $6p\ ^3D_2$ 157826·3	*c* $6p\ ^3D_3$ 147555·7	*d* $6p\ ^1D_2$ 159135·2
				913·1	10270·6		
A	$6s\ ^3P_0$	201079·0	546·2	42339·6 (7)			
B	$6s\ ^3P_1$	200532·8	8532·8	41793·1 (6)	42706·5 (4)		41397·8 (0)
C	$6s\ ^3P_2$	192000·0		33260·8 (1)		44444·3 (5)	
D	$6s\ ^1P_1$	200340·8		41601·1 (4)			41205·9 (9)
E	$5d\ ^3F_2$	201113·7		42373·6 (2)	43288·3 (3)		
F	$5d\ ^3D_1$	199981·7		41243·4 (3)	42155·2 (3)		
G		201272·3		42532·5 (1)			42137·6 (6)
H		202768·3			44941·3 (3)		
J		198423·1			40597·5 (3)		

Odd terms \ Even terms				*e* $6p\ ^3P_0$ 172347·4	*f* $6p\ ^3P_1$ 160857·9	*g* $6p\ ^3P_2$ 160889·7	*h* $6p\ ^1P_1$ 169691·8	*i* 160585·6
				11489·5	- 31·8			
A	$6s\ ^3P_0$	201079·0	546·2		40221·0 (4)			
B	$6s\ ^3P_1$	200532·8	8532·8	28185·6 (4)	39674·7 (8)	39643·5 (6)		
C	$6s\ ^3P_2$	192000·0			31142·5 (4)	31109·9 (6)		
D	$6s\ ^1P_1$	200340·8			39482·9 (4)			
E	$5d\ ^3F_2$	201113·7			40255·3 (0)		31421·3 (4)	40528·0 (3)
F	$5d\ ^3D_1$	199981·7					30290·3 (3)	39396·4 (5)
H		202768·3			41910·9 (4)	41878·9 (8)		
I		204954·8			40097·0 (4)	40065·8 (9)		
J		198423·1					28731·5 (2)	37837·2 (5)

fication; these will be presented in a future paper. The terms are designated arbitrarily as *A*, *B*, *C*, *D*, ... when they are supposed to be odd, or as *a*, *b*, *c*, *d*, ... when they are even. The suggested assignment for these terms also is given at the left and top of the table. In assigning these levels, greater consideration was paid to a comparison with the corresponding levels in other isoelectronic spectra than to the

indication of the intensities of the lines in the various levels, for, on account of the expected large deviations from the normal *LS* coupling, the interval and intensity rules are liable to be departed from to a very great extent.

One peculiar feature according to the above assignment of the terms is that $6p\ ^3P$ is partially inverted, as is observed also in Te III, but not in Sn I or Sb II. The term $6p\ ^3D$ is, however, remarkably regular in the whole row of these spectra, and it might be significant to notice that this term is, according to Hund, the deepest triplet term arising from the $6p$ configuration.

Table 5. Lines of I IV

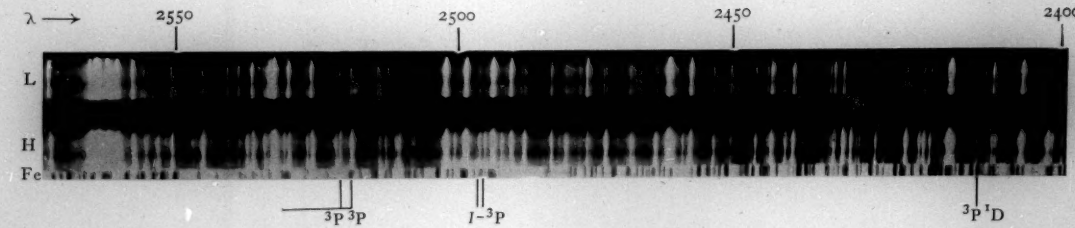
λ	ν	Classification	λ	ν	Classification	λ	ν	Classification
3546·90 (4)	28185·6	*B–e*	2545·67 (8)	39270·6		2418·82 (3)	41329·9	
3479·51 (2)	28731·5	*J–h*	2537·54 (5)	39396·4	*F–i*	2418·45 (2)	41336·2	
3300·44 (3)	30290·3	*F–h*	2531·98 (4)	39482·9	*D–f*	2414·85 (0)	41397·8	*B–d*
3224·98 (6)	30999·8		2521·72 (6)	39643·5	*B–g*	2403·61 (3)	41591·4	
3213·48 (6)	31109·9	*C–g*	2519·74 (8)	39674·7	*B–f*	2403·05 (4)	41601·1	*D–a*
3210·12 (4)	31142·5	*C–f*	2516·82 (2)	39720·7		2392·00 (6)	41793·3	*B–a*
3181·64 (4)	31421·3	*E–h*	2513·74 (3)	39769·4		2387·11 (8)	41878·9	*H–g*
3170·11 (4)	31535·6		2511·04 (3)	39802·1		2385·28 (4)	41910·9	*H–f*
3153·86 (3)	31698·1		2501·38 (2)	39965·9		2376·46 (7)	42066·5	
3151·61 (1)	31720·7		2496·05 (3)	40051·2		2372·45 (6)	42137·6	*G–d*
3069·17 (4)	32572·6		2495·14 (2)	40065·8	*I–g*	2371·46 (3)	42155·2	*F–b*
3005·67 (1)	33260·8	*C–a*	2493·20 (4)	40097·0	*I–f*	2367·75 (5)	42221·3	
2931·11 (3)	34118·8		2489·24 (5)	40160·8		2361·13 (7)	42339·6	*A–a*
2917·33 (5)	34267·9		2485·51 (4)	40221·0	*A–f*	2359·24 (2)	42373·6	*E–a*
2910·97 (4)	34342·8		2483·39 (0)	40255·3	*E–f*	2353·45 (1)	42477·8	
2885·15 (3)	34650·1		2475·71 (0)	40380·2		2350·42 (1)	42532·5	*G–a*
2864·68 (6)	34897·7		2475·35 (8)	40386·1		2340·84 (4)	42706·5	*B–b*
2839·42 (2)	35208·1		2466·96 (3)	40523·5		2309·38 (3)	43288·3	*E–b*
2818·45 (3)	35470·1		2466·68 (3)	40528·0	*E–i*	2280·05 (2)	43845·1	
2736·64 (1)	36530·3		2462·46 (3)	40597·5	*J–b*	2249·30 (5)	44444·3	*C–c*
2652·23 (8)	37692·9		2434·85 (6)	41057·8		2238·11 (1)	44666·6	
2642·11 (5)	37837·2	*J–i*	2426·10 (9)	41205·9	*D–d*	2224·43 (3)	44941·3	*H–b*
2640·77 (4)	37856·4		2423·89 (3)	41243·4	*F–a*			

Further, if the identification of $6s\ ^1P_1$ is correct, it is observed to be deeper than $6s\ ^3P_2$. This indicates a tendency to approach, together with the terms $6s\ ^3P_1$ and $6s\ ^3P_0$, to the limit $5p\ ^2P_{\frac{1}{2}}$ of the next higher ion; there is thus an intermingling of the triplet and the singlet terms of the $6s$ configuration.

Two intense lines, ν 40386·1(8) and ν 44444·3(5) might be suggested as probably forming the combinations $5d\ ^3F_4$–$6p\ ^3D_3$ and $6s\ ^3P_2$–$6p\ ^3D_3$.

The term-values given in table 4 are based on the value 192000 assumed for the term $6s\ ^3P_2$, and obtained by extrapolation from the corresponding values in Sn I, Sb II, Te III; this value might serve at least as well as one arbitrarily chosen.

Finally, a list of the lines due to the spectrum of I IV, along with the classification suggested for some of these in the present work, is given in table 5.



L, Discharge-tube spectrum of iodine under lower excitation. H, Discharge-tube spectrum of iodine under higher excitation. Fe, Spectrum of the iron arc for comparison.

§ 4. ACKNOWLEDGMENTS

In conclusion, I have great pleasure in expressing my indebtedness to Dr K. R. Rao for his kind guidance and helpful suggestions throughout the progress of this work.

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THE EFFECT OF DISSOLVED AIR ON THE SPECIFIC HEAT OF WATER OVER THE RANGE 15° TO 20° C.

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ABSTRACT. The effect of dissolved air on the specific heat of water is calculated thermodynamically from the solubility data, for the case when no air is liberated, either completely or in the form of bubbles. It is shown that the specific heat of water saturated with air at 20° C. under normal atmospheric pressure exceeds that of air-free water by 6×10^{-6} cal./g.

§ 1. INTRODUCTION

In a recent paper by Laby and Hercus[1] it was shown that the liberation of air from water on heating could have no significant effect on the specific heat. Dr Jessel, in the discussion, suggested that the air might affect the specific heat without being liberated. In reply it was stated, on thermodynamic grounds, that the difference could not exceed 1 in 100,000. This paper gives a detailed statement of the grounds for that conclusion.

§ 2. THE HEAT OF SOLUTION OF AIR IN WATER

L The molar latent heat L of evaporation of air from a solution in water to air in equilibrium with it is given by:

$$L = RT^2 . \partial \log K / \partial T,$$

K where K is the constant of Henry's law given by $p_A = Kx$, x being the mol-fraction of air dissolved under a pressure of p_A cm. of mercury. From the values of K given in the table[2]

Temperature (° C.)	$10^{-7} \times K$	Temperature (° C.)	$10^{-7} \times K$
14	4·525	19	4·964
15	4·612	20	5·044
16	4·701	21	5·130

we have $L_{15} = 3150$ cal./mole, $L_{20} = 2810$ cal./mole.

L′ These values include the work done against the external pressure; by subtracting RT we obtain the corresponding changes L' in internal energy:

$$L'_{15} = 2570 \text{ cal./mole}, \qquad L'_{20} = 2230 \text{ cal./mole}.$$

§3. COMPARISON OF SPECIFIC HEATS

By consideration of the following cycle it is possible to compare the specific heat, S_2 international cal./g.,* of water containing enough air to saturate it at 20° C. under normal atmospheric pressure, with the specific heat, S_3 international cal./g. of air-free water. Taking one gram of water, the amount n of air involved is, from the table above quoted, $8{\cdot}4\times10^{-8}$ mole.

S_2 S_3 n

(*a*) Cool the aerated water from 20° C. to 15° C. The loss of entropy from the system is $\int_{288}^{293}\frac{S_2}{T}\,dT$.

(*b*) Release the pressure isothermally from normal atmospheric pressure π to the pressure p_1 at which the solution is saturated at 15° C. Here $\pi/p_1=1{\cdot}094$. The gain in entropy B in this stage is calculable from the Maxwell relation

π p_1

$$\left(\frac{\partial\phi}{\partial p}\right)_T=-\left(\frac{\partial v}{\partial T}\right)_p,$$

but it is offset by a corresponding gain later since, as Chappuis's experiments[3] have shown, the density of water is not appreciably affected by dissolved air.

(*c*) Suppose the water surface to be provided with a semi-permeable membrane freely permeable to air but not to water vapour. By withdrawing a piston from the surface, allow the air to come out of solution until, when the pressure is reduced from p_1 to p_0, a negligible amount of air remains in solution; p_0 disappears in the final equations and so may be arbitrarily small. If this is carried out isothermally, the work done by the air in expanding to volume v_0 is $\int_0^{v_0}p\,dv$. At any stage in this process, out of the n moles of air an amount proportional to p, say kp, is in solution and the remainder, $n-kp$, occupies as a gas a volume v under pressure p.

p_0 v_0 k

Hence
$$pv=(n-kp)\,RT,$$
$$p=\frac{nRT}{v+kRT},$$
$$\int_0^{v_0}p\,dv=nRT\log_\epsilon\frac{v_0+kRT}{kRT}=nRT\log_\epsilon\frac{p_1}{p_0}.$$

The gain in entropy in this stage is therefore

$$n\frac{L'_{15}}{288}+nR\log_\epsilon\frac{p_1}{p_0}.$$

(*d*) Separate the water from the air. Increase the pressure on the water from p_1 to π, isothermally, with a loss of entropy B—the inverse of stage (*b*). Then heat the air-free water to 20° C. Heat the air under pressure p_0 to 20° C. The entropy gained is

$$-B+\int_{288}^{293}\frac{7{\cdot}02n}{T}\,dT+\int_{288}^{293}\frac{S_3}{T}\,dT.$$

* It is most convenient to define the other heat quantities in terms of the 15° C. calorie.

(*e*) Compress the air isothermally from pressure p_0 to the pressure p_0' at which it is in equilibrium with the infinitesimal amount of air remaining in solution. The loss of entropy is $nR \log_\epsilon (p_0'/p_0)$, where $p_0'/p_0 = 1{\cdot}0936$.

(*f*) Compress the air isothermally into solution at 20° C. through a semi-permeable membrane. The loss of entropy—compare stage (*c*)—is

$$\frac{nL'_{20}}{293} + nR \log_\epsilon \frac{\pi}{p_0'}.$$

Equating to zero the whole entropy-loss for the cycle we find that

$$\int_{288}^{293} \frac{S_2 - S_3}{T}\, dT + nR \log_\epsilon \frac{\pi}{p_1} + n\frac{L'_{20}}{293} - n\frac{L'_{15}}{288} - 7{\cdot}02\, n \log_\epsilon \frac{293}{288} = 0,$$

$$\int_{288}^{293} \frac{S_2 - S_3}{T}\, dT = 8{\cdot}4 \times 10^{-8}\left[-1{\cdot}986 \log_\epsilon 1{\cdot}094 - \frac{2230}{293} + \frac{2570}{288} + 7{\cdot}02 \log_\epsilon \frac{293}{288}\right]$$

$$= 1{\cdot}04 \times 10^{-7}.$$

Assuming as a sufficient approximation that $(S_2 - S_3)$ does not vary with temperature, we find that

$$S_2 - S_3 = 1{\cdot}04 \times 10^{-7}/\log_\epsilon (293/288)$$

$$= 6{\cdot}0 \times 10^{-6}.$$

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THE RANGES OF α PARTICLES IN PHOTOGRAPHIC EMULSIONS

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ABSTRACT. Numerous α-particle tracks on Ilford *R* plates have been measured. From measurements of the tracks of a homogeneous group of α particles of range *R*, a distribution curve may be drawn, from which a length *L*, known as the extrapolated length of the tracks, can be determined. The ratio L/R is shown to be constant to within 1 per cent for α particles of various ranges, and hence *R* can be found for a group of unknown tracks if *L* is measured. The method is applied to determine the ranges corresponding to the tracks produced by the disintegration of boron and lithium under slow-neutron bombardment. These are found to be $1{\cdot}14 \pm 0{\cdot}02$ cm. in air and $6{\cdot}64 \pm 0{\cdot}06$ cm. in air, respectively. Samarium has also been investigated, and is found to emit α particles of range $1{\cdot}13 \pm 0{\cdot}02$ cm. in air. Other particles from samarium, of longer range, have also been found.

§ 1. INTRODUCTION

It has been known for many years that it is possible to record the tracks of α particles in a photographic emulsion. In earlier papers[1,2] estimates are given of the mean length of such tracks for α particles of known energy, and these accord quite well with recent measurements. The photographic method of recording heavy particles has recently been shown to have important applications, and the technique has been improved. It has therefore become necessary to make a closer study of the relation between the lengths of the tracks measured in the emulsion and the corresponding ranges in air. The purpose of the present paper is to discuss this relation and to decide the degree of accuracy with which it is possible to determine the range in air of a group of α particles, on the basis of measurements of the length of the tracks produced in the emulsion.

If a homogeneous group of α particles is caused to traverse the emulsion, the tracks produced by the individual α particles are not all of the same length. The variations have been shown in a previous paper[3] to be due to the following causes: (*a*) straggling of the ordinary type; (*b*) additional straggling introduced by the inhomogeneity of the medium; (*c*) the difference between the actual distance traversed by the particle and the measured distance between the end grains; (*d*) uncertainty whether the whole path of the particle is contained within the emulsion.

The variations due to these four factors are in increasing order of magnitude. For α-particle tracks, and short tracks generally, (*d*) may be excluded; it becomes of importance only in the case of long tracks for which the number of grains per unit length is small, such as the proton recoil tracks produced by neutrons[3].

Reasons were given in the previous paper[3] for supposing that the combined effect of (*a*), (*b*), and (*c*) would be very appreciable. Thus for the α particles from thorium C′, having a range in air of 8·6 cm., one would expect to find differences amounting to 20 per cent between the maximum and minimum measured lengths in, say, 100 measurements. This conclusion is confirmed by the observations. In a group of 400 thorium C′ α-particle tracks recently measured, the maximum and minimum lengths were 31·0 and 22·9 scale divisions, the extent of variation being thus 26 per cent of the maximum. Smaller groups show a variation of about 20 per cent.

It is to be observed that the discrepancy (*c*) represents the amount by which the end grains fall short of being exactly at the ends of the true path, and this amount is independent of the length of the track. Thus the actual magnitude of the error introduced will be approximately the same for particles of all ranges, so that the relative difference between the maximum and minimum measured lengths will be greater, the smaller the range of the particles. This conclusion also is borne out by the measurements. In 200 measurements of the tracks produced by thorium C α particles, having a range in air of 4·7 cm., the minimum shows a variation of 35 per cent with respect to the maximum. In 300 measurements of the short-range α particles of samarium, having a range in air of 1·13 cm., the maximum and minimum measured lengths are 4·0 and 1·2 scale divisions.

In determining, therefore, the range which a particle would have in air, by measuring its track in the emulsion, large errors are unavoidable. It was for this reason that the method was found unsuitable for determining the detailed distribution of neutron energies from measurements of the tracks of recoil protons[3]. Where, however, it is possible to measure a large number of tracks produced by particles all of the same energy, much higher accuracy is attainable in determining the corresponding range in air. We have examined this question on the basis of large numbers of measurements of the tracks produced by α particles of known energy.

§ 2. DEFINITION OF *L*

The problem before us is twofold. Firstly, we have to determine from the measurements a single representative value L which will define the length of the tracks. We have secondly to find the relation between L and the range R in air. The selection of the best representative value is by no means easy. Even in air the individual ranges of α particles of the same energy show small variations due to straggling, and the value to be taken as the range in air has to be defined. Thus we have the extrapolated range, derived from the Bragg ionization curve, which differs from the mean range. Either of these representative values may be taken as a measure of the range in air, and one could suggest others, such as the most probable range.

For the tracks in the emulsion several such choices are possible. The most obvious suggestion is to define L as the mean of a large number of measurements. The mean of a set of observations, however, is only a satisfactory statistic when the

conditions are satisfied (*a*) that the observations constitute a true random sample of all possible observations, and (*b*) that the distribution curve of the observations is symmetrical. In the present case neither condition is satisfied. The measurements cannot form a truly random sample, for one is obliged to select tracks for measurement which are horizontal or nearly so, and of which the end points are well-defined. Tracks which do not satisfy these criteria are rejected. There is reason to think that such a selected sample approximates to a random sample, but it is evidently not wholly so. The selective character of the measurements is apparent in the differences which appear between similar groups of tracks measured by different observers. The position of the maximum of the distribution curve may be slightly different, and one observer's measurements may show a preponderance of shorter tracks as compared with another's.

If the true paths of the particles in the emulsion could be measured one would presumably obtain a distribution curve approximately symmetrical about the mean

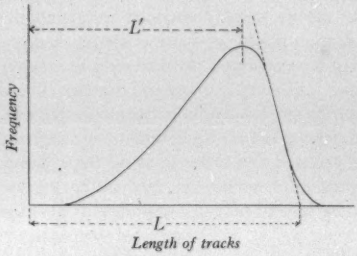

Figure 1. General form of distribution curve.

length. The actual measured distance, however, is the distance between the end grains, which do not as a rule lie at the extreme points of the path. It follows that the number of measurements which fall short of the (unknown) mean will be greatly in excess of those which exceed it. The point was considered in the previous discussion[3], and it was pointed out that the probability of a given defect of the measured length with respect to the true path is not a symmetrical function. In general, it appears that if the frequency-distribution of the measured lengths be plotted, it will have the general form shown in figure 1, and the results of the actual measurements confirm this.

The next suggestion, therefore, is to choose the value L' which corresponds to the peak of the distribution curve; and this amounts to a choice of the mode or most probable length. For reasons already stated, L' will differ from the true mean path p by an approximately constant amount, irrespective of the length of the path. Thus the ratio L'/p will decrease with p. The value of p is of course unknown, but we may suppose it to be proportional to R, the range in air. Thus the ratio L'/R will decrease with R. This is seen from table 1, where the ratio has been calculated for known α particles of different ranges.

L'

p

Table 1

Source of α particles	Thorium C′	Radium C′	Thorium C	Uranium II
Extrapolated range in air (cm.)	8·623	6·945	4·746	3·28
L'	61·24	48·18	32·81	21·58
L'/R	7·014	6·937	6·913	6·580

A further objection to the use of L' is that the maximum of the curve is not a point which can be determined with great accuracy. Occasionally, owing to the inevitable fluctuations in a limited group of measurements, the curve shows two peaks. Even where the peak is well-defined, its position as determined by different observers may vary slightly.

We have therefore come to the conclusion that the best representative value is that obtained by extrapolating the curve, and determining the point of intersection on the x axis. If the curves actually obtained were smooth no difficulty would arise, and the extrapolation would be made as shown in figure 1. Actually, however, a limited group of measurements gives an irregular curve, and the descending portion generally shows subsidiary maxima and minima. These irregularities are so large that extrapolation by eye estimation is impracticable, and if it were attempted the value of L would depend largely upon individual judgment. It is necessary to adopt some standard procedure in order to avoid these personal differences. The device we have adopted is to replace the descending portion of the curve by a straight line through the plotted points, computing its position by the principle of least squares. Thus if $x_1, y_1; x_2, y_2; \ldots$ are the coordinates of the n points, and $y=a+bx$ is the straight line, the values of a and b are those for which $(y_r-y)^2$ is a minimum. These values are calculated from the formulae

$$a=(\Sigma x\Sigma xy-\Sigma y\Sigma x^2)/\{(\Sigma x)^2-n.\Sigma x^2\},$$
$$b=(\Sigma x\Sigma y\ \ -n.\Sigma xy)/\{(\Sigma x)^2-n.\Sigma x^2\}.$$

We then have for the point of intersection on the x axis, $L=-a/b$.

This procedure is admittedly empirical, but it gives a value for L, the length of the tracks, which is definite, unambiguous, and free from personal errors of estimation. Further, the determination of L from a group of measurements is not unduly laborious, and it is found in practice that L has a much more nearly constant value than L'. The values of L deduced from different groups of measurements are remarkably constant, although the shape of the curves varies considerably.

§ 3. DETERMINATION OF L

The measurements of the lengths of the tracks show two characteristic types of error. Firstly, the plates are never wholly free from background grains which do not belong to the tracks at all. If a background grain happens to lie just beyond the end of a track it may be mistaken for an end grain, and the measured length will be greater than it should be. Nearly all our groups of measurements show one or two

tracks of excessive length which we believe to be due to this cause, and these have accordingly been ignored in the determination of L. These long tracks sometimes appear on the distribution curve as a small peak well to the right of the main curve. This can be seen in figure 2.

Another type of error in the measurements is of interest. The grains are of very small diameter, of the order of $0{\cdot}3\mu$, and therefore what is seen in the microscope is scarcely a geometrical image of a grain, but rather a small diffraction circle. A scale division corresponds approximately to 2μ, and the readings involve the estimation of the position of the centres of the diffraction circles which correspond to the end grains. When the diffraction circle is near a scale division there is an apparent coalescence which results in an excess of measurements which are read as an integral number of scale divisions. In addition, there are personal idiosyncrasies in the estimation of tenths which cannot be wholly eliminated; these have been discussed

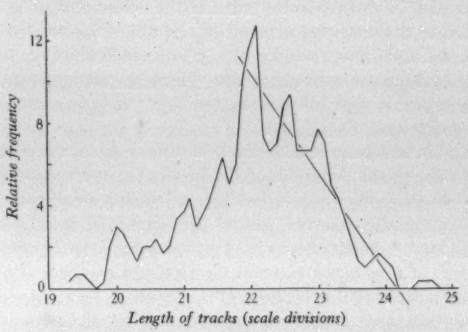

Figure 2. Distribution curve of tracks produced by radium C′ α particles.

at some length by Yule[4]. We find, therefore, that the detailed distribution of the measurements is somewhat uneven, and if the frequency of occurrence is plotted directly against the measured length in scale divisions, peaks tend to occur at the whole numbers, and to a lesser extent at the mid points of the divisions. Although we have been conscious of the existence of these tendencies, and have therefore been on our guard against the careless estimation of tenths, we find that they are not wholly eliminated with increasing experience. The conclusion to be drawn is that the limit of accuracy in the measurement of the lengths of individual tracks has been reached, at least with the present optical equipment.* We estimate the probable error of an individual measurement to be of the order of 1/5 of a scale division, or $0{\cdot}4\mu$.

We have therefore thought it proper to smooth out minor irregularities in the curves by the device of a moving average. The direct curve would be given by

* A dry objective of the highest available nominal aperture has been used throughout, for when large areas of the plate have to be traversed the use of an immersion objective is impracticable, and in any case it is undesirable to have oil on the gelatine surface.

plotting the number of tracks against the measured length. The smoothed curve is obtained by plotting the mean of three consecutive ordinates against the abscissa of the central ordinate. This is a well-known statistical device which has the effect of reducing minor irregularities while accentuating the general trend of the curve. It has been adopted for all the curves—indeed an even wider moving average would be justifiable, say one of five consecutive ordinates.

Before plotting the frequency curves it is necessary to correct the measurements for the inclination of the tracks. If a track is not in the horizontal plane, the vertical distance between the two ends is measured by means of the vertical motion of the microscope. This measurement can be made to 1μ. Owing to the refraction of light in the gelatine, the true vertical separation is greater than the measured distance. If the objective used were of small nominal aperture, so that the rays were all approximately parallel to the axis, it would suffice merely to multiply the readings by a factor equal to n, the refractive index of the gelatine. With a large-aperture objective, however, the image is produced by rays of which some make large angles with the axis, and the apparent depth of a grain is accordingly reduced. The objective is corrected for use with uncovered objects, so that when a grain at some depth in the emulsion is under observation the objective is, in effect, over-corrected for spherical aberration.

When the grain is only at a small depth in the emulsion, the over-correction is insufficient to destroy the definition of the image, but the apparent depth of the grain is less than that which would be observed with a small-aperture objective. The factor by which the observed vertical depth must be multiplied in order to obtain the true depth is greater than n, and can be approximately calculated by considering the path of a mean ray between the axial and marginal rays. It may also be estimated by measuring the thickness of the emulsion by independent methods. With the present objective the factor is approximately 2, and we have used the value 2·0 in the present measurements. The error in the measurement of depth is relatively much greater, however, than that in the measurement of length, so that only those tracks have been included for which the correction on account of inclination is small. In order to apply the correction quickly and accurately, a graphical method has been used.

§ 4. THE DEPENDENCE OF L UPON VARIOUS FACTORS

It is necessary to know whether the length L corresponding to a given group of particles, defined and determined as described, is a constant quantity. Its value might conceivably depend upon (*a*) the plate used, and the mode of development; (*b*) the observer; (*c*) the number of measurements included in the group. We now consider these separately.

(*a*) *The plate.* Ilford *R* plates, originally designed for recording these tracks, have been used throughout. The properties of these plates are remarkably constant. Measurements have been made upon plates of the early batches (August 1934), and on successive batches of plates up to the present time, and no significant differences can be detected. In particular the value of L for a given group of particles has not

varied. Moreover, the value of L is practically unaffected by changing the time of development, within wide limits. A standard metol-hydroquinone developer is used, and development is allowed to take place slowly to secure uniformity. The usual time of development is 18 min. at 18° C. Three plates were exposed in exactly the same way to a source of thorium (B+C), the α particles being allowed to fall almost tangentially on the plates in a vacuum. These plates were developed for 13, 18, and 23 min. The plates show considerable difference in appearance, for the number of background grains increases with the time of development. Also the apparent density of the tracks increases with the time of development. In an undeveloped plate some of the affected grains are only partially reduced to silver by the action of the developer, and hence are less easily seen. They may, indeed, be invisible, so that the mean number of grains per unit length is found to be less for tracks on an underdeveloped plate. A consequence of this is that an underdeveloped plate may show a preponderance of relatively shorter tracks. The end point of the distribution curve, however, as defined by L, is found to be the same for all three plates, within the limits of error. This is understandable when one observes that even an underdeveloped plate will show some tracks which approach the maximum length. Extremely underdeveloped plates, however, will of course not give satisfactory results, for then the variations between individual measurements become very large.

(*b*) *The observer.* The measurements on which the present paper is based have been made by two observers, but the measurements have been kept separate throughout. We can find no systematic differences in the value of L between the two sets of observations. This point having been established, both sets have been combined in order to obtain the final results.

(*c*) *The number of measurements.* The value of L will obviously depend on the number of measurements, for in a small group the random departures from the ideal distribution are relatively more important. The largest groups number some 400 measurements, whilst several curves have been drawn with groups numbering upwards of 100. The smoothness of the curves increases with the number of measurements, but to measure very large numbers of tracks is in many cases not feasible. We have, for example, the tracks produced by the transformation of lithium under slow neutron bombardment, § 8. The best plate showing these tracks had an exposure about as long as would normally be practicable. The source of neutrons consisted of beryllium and radon of initial strength 150 millicuries, and the exposure lasted four days. Even on this plate, however, the tracks are very sparse, and up to the present we have only been able to accumulate 117 satisfactory measurements. It is unlikely that if the method were applied to other nuclear reactions the tracks obtained would usually be more numerous than these. Since the main interest of the method lies in its application to the determination of the ranges corresponding to unknown tracks of this kind, we have limited the observations to groups of not more than a few hundred measurements.

The minimum number of measurements required to give a reproducible value of L may be taken as 100. Smaller groups have not given satisfactory results.

§ 5. MIXED GROUPS OF PARTICLES

Uranium emits two groups of α particles, corresponding to the isotopes uranium I and uranium II. The ranges of these particles in air are 2·7 and 3·3 cm. It is not possible to determine by inspection whether any given track belongs to the shorter or the longer group, so that the measurements include both kinds of track in approximately equal numbers. In the case of thorium (B + C) the ranges 4·7 and 8·6 cm. of the two groups of α particles emitted differ so widely that any track can be assigned immediately to its proper group, so that the difficulty does not arise.

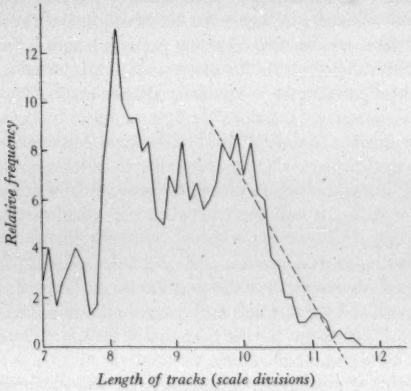

Figure 3. Distribution curve of tracks produced by uranium α particles.

The curve for uranium is shown in figure 3. If one were unaware of the origin of the tracks the existence of two groups could be argued from the curve, but not with any degree of certainty. The value of L computed in the usual way clearly applies to the longer-range group, and that corresponding to the shorter-range group cannot be determined except as a rough estimate. The example of uranium makes it clear that the present method is not adapted for separating groups of particles of closely similar ranges. We consider that two groups of particles should differ in range by at least 1 cm. of air in order to be clearly and unambiguously resolved by the present method.

§ 6. RELATIONSHIP BETWEEN L AND R

The extrapolated length L for any group of α-particle tracks is found to be proportional to R, the extrapolated range in standard air. α particles of four ranges have been used, and the results are collected in table 2. We have taken the values of R from the most recent determinations[5]. The table contains 17 determinations of L/R. These determinations refer to plates which have received very different treatment; some are extremely clean and others show a good deal of background.

The ranges of the α particles vary between 3·3 and 8·6 cm. in air, and the number of measurements in the individual groups varies between 90 and 420. It is satisfactory to find, therefore, that L/R is constant to what must be regarded as a fair degree of accuracy. The maximum and minimum values of L/R are 7·662 and 7·397, so that the deviation from the mean is never more than 2 per cent. In order to find

Table 2

Source of α particles	Series number	Number of tracks	R	L	L/R	Notes
Thorium C′	1	130	8·623	65·05	7·543	Plate I, developed in 13 min.; measurements by T.
Thorium C′	2	90	8·623	65·42	7·587	Plate I, developed in 13 min.; measurements by D.
Thorium C′	3	100	8·623	65·94	7·647	Plate II, developed in 18 min.; curve showing two maxima.
Thorium C′	3	100	8·623	64·70	7·504	
Thorium C′	4	100	8·623	64·51	7·481	Plate III, developed in 23 min.
Thorium C′	5	420	8·623	64·83	7·519	Total of all measurements.
Radium C′	6	110	6·945	52·71	7·590	Measurements by T.
Radium C′	7	90	6·945	52·10	7·502	Measurements by D.
Radium C′	8	200	6·945	52·71	7·590	Total of all measurements.
Thorium C	9	90	4·746	36·06	7·597	Plate I, developed in 13 min.; measurements by T.
Thorium C	10	119	4·746	36·36	7·662	Plate II, developed in 18 min.; measurements by D.
Thorium C	11	100	4·746	36·06	7·597	Plate II, developed in 18 min.
Thorium C	12	99	4·746	35·32	7·441	Plate III, developed in 23 min.
Thorium C	13	408	4·746	36·01	7·588	Total of all measurements.
Uranium II	14	58	3·28	—	—	Plate I, not a satisfactory curve; only a few tracks were obtainable on this plate.
Uranium II	15	179	3·28	24·26	7·397	Plate II.
Uranium II	16	237	3·28	24·76	7·550	Total of all measurements.
Uranium II	16	237	3·28	24·28	7·404	Total with alternative extrapolation.

a suitable mean, we have taken the four groups of which each contains the total measurements for each kind of track. By plotting L against R, points are obtained which lie very closely on a straight line. The best straight line amongst these points is computed by the method of least squares, and its slope gives what is probably the best value of the ratio. In view of the slight ambiguity in the value of L/R for the uranium tracks, equal weight has been given to both values, which are the last two values in table 2.

The mean value of L/R so determined is found to be 7·543. If x represents the probable error in this value, about half the determinations ought to have deviations greater than x, and about one-sixth ought to have deviations greater than $2x$. Out of the 17 values in the table, 12 lie well within 1 per cent of the mean, and no deviation exceeds 2 per cent. It follows that probably x is appreciably less than 1 per cent of the mean value.

If x is deduced in the usual way from the deviations, the value found is 0·053. One must also take into account the fact that 17 is rather a small number of determinations upon which to base an estimate of x. Statistical theory shows that the

probable error in x will be $[0{\cdot}51/\sqrt{(17)}].x$, or 0·007. If we assume the limit of error in x to be three times the probable error, we get 0·074 as the maximum possible estimate of x, which is almost exactly 1 per cent of the mean. We have therefore adopted ± 1 per cent as a safe estimate of the probable error in a single determination of L/R.

It is now possible to determine the range in air corresponding to any unknown group of tracks by applying the relationship $L/R = 7{\cdot}543 \pm 0{\cdot}075$. We have therefore used this to determine (*a*) more accurate values of the ranges corresponding to the tracks which result from the disintegration of boron and lithium by slow neutrons; and (*b*) the range of the α particles of samarium.

§ 7. BORON-DISINTEGRATION TRACKS

It has been shown previously[6,7] that boron, when bombarded by slow neutrons, disintegrates according to the following scheme:

$$B^{10} + n^1 \rightarrow Li^7 + He^4.$$

Tracks have been obtained which correspond in length to the total range of the two resultant particles. The previous best estimate of this total range was $1{\cdot}1 \pm 0{\cdot}1$ cm. in air, which agrees with the measurements of Kurtchatow, Kurtchatow and Latychew in a Wilson chamber[8].

We have now computed the extrapolated length of the tracks from a group of 329 measurements made on the best plate. Only horizontal tracks have been measured, to avoid errors due to inclination. The value of the range in air is found to be 1·14 cm. Owing to the shortness of the tracks the accuracy with which L can be determined for these tracks is doubtless somewhat less than for the α-particle tracks already considered. Also, though L/R has been shown to be constant for α particles of range between 3·3 and 8·6 cm., it is perhaps unsafe to extrapolate this result to extremely small ranges. To take these considerations into account the value assigned to the probable error must be increased. We take the following value to be the best at present:

$$R = 1{\cdot}14 \pm 0{\cdot}02 \text{ cm.}$$

We have now to determine, if possible, the energy associated with this range. The total energy E is divided between the particles in the inverse ratio of their masses, so that the velocities of the particles are known in terms of E. If then the {range, velocity} relation is known for each kind of particle, the total range corresponding to E can be found. Conversely, one can find by trial the value of E corresponding to the given range.

Unfortunately the {range, velocity} relation for lithium recoil atoms is unknown, and the uncertainty arising from this cause is greater than that involved in the measurement of R. One may, however, make use of the formula

$$R = km z^{-n} f(v) \qquad \text{.....(1),}$$

where m, z, and v represent the mass, nuclear charge, and velocity of the particle, and k is a constant. For fast protons and α particles we may put $n = 2$, for an

α particle has approximately the same range as a proton of the same velocity. For much heavier recoil atoms, N^{14}, O^{16}, O^{17}, A^{40}, F^{19}, the formula has been shown to represent the observations approximately, with n equal to $\frac{1}{2}$ [9,10]. The best one can do, therefore, in the absence of observations on lithium recoil atoms, is to use the formula and assume n to be somewhat less than 2. Calculation with various values of n gives an idea of the uncertainty involved.

This procedure leads to the following estimate for the total energy released in the reaction

$$E = 2{\cdot}25 \pm 0{\cdot}10 \times 10^6 \text{ eV}.$$

This value agrees, within the limits of error, with that which may be deduced from our present knowledge [11,12,13] of the masses of the particles involved in the reaction.

§ 8. LITHIUM-DISINTEGRATION TRACKS

It has already been reported [7] that tracks are obtained which correspond to the reaction

$$Li^6 + n^1 \rightarrow He^4 + H^3.$$

An example is shown in figure 4. The previous estimate of the total range for these tracks, $6{\cdot}9 \pm 0{\cdot}2$ cm. in air, depended upon the position of the maximum of the distribution curve, and only a small group of measurements was available. For

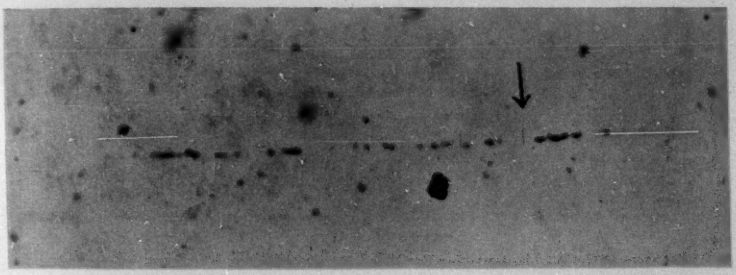

Figure 4. Disintegration of lithium by slow neutrons. The arrow shows the point of disintegration.

the present determination we have limited ourselves to tracks for which the inclination to the horizontal is small, and whose end points are clear and unambiguous. The tracks are infrequent, and the number of satisfactory measurements so far obtained is 117. These are found to give the distribution curve shown in figure 5, and the value of the range in standard air deduced in the usual way is

$$R = 6{\cdot}64 \pm 0{\cdot}06 \text{ cm}.$$

In this result the probable error given is that which is inherent in the determination, according to the considerations already outlined. There is another source of error of unknown, though probably small, magnitude, namely the fact that we do not know whether the ratio L/R is the same for hydrogen nuclei as for α particles.

In other words, it is not known whether the stopping-power of the emulsion relative to air is the same for the two kinds of particle, and there is no means of determining this in the absence of sources giving homogeneous groups of hydrogen nuclei. Experiments have been made with the protons ejected from paraffin by polonium α particles, which lead to the view that the difference of stopping-power is not large. In any case, there are no accurate data available on the {range, energy} relation of H^3 particles of the range occurring in this reaction, so that further discussion of this source of error would be premature.

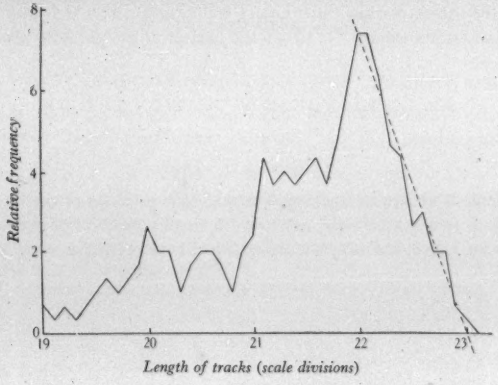

Figure 5. Distribution curve of the lithium-disintegration tracks.

To calculate the total energy released in the reaction, we have assumed the validity of formula (1), and deduced the {range, energy} relation from that which is known for protons. The value so derived is

$$E = 4{\cdot}3 \pm 0{\cdot}1 \times 10^6 \text{ eV}.$$

If we assume the recently proposed values for the masses of neutral atoms we have [11]

$$n^1 = 1{\cdot}0083 \pm 0{\cdot}0003, \qquad H^3 = 3{\cdot}0161 \pm 0{\cdot}0003,$$
$$Li^6 = 6{\cdot}0163 \pm 0{\cdot}0006, \qquad He^4 = 4{\cdot}0034 \pm 0{\cdot}0004.$$

The balance of energy in the reaction is thus seen to be $0{\cdot}0051 \pm 0{\cdot}0008$ mass units, or $4{\cdot}7 \pm 0{\cdot}8 \times 10^6$ eV., which is in good agreement with the value derived above.*

§ 9. THE PARTICLES FROM SAMARIUM

Several papers have been published [15, 16, 17, 18] on the radioactivity of samarium. The general result is that samarium emits α particles of range about 1·1 cm. and

* Budnizki, Kurtschatow, and Latychew [14] give the ranges of the He^4 and H^3 particles as 2·0 and 6·5 cm. in air, as measured in a Wilson chamber. If momentum is conserved, the ratio of the ranges should be much greater. Furthermore the total energy, as deduced from the range of the α particle, is $7{\cdot}9 \times 10^6$ eV., which is clearly too large.

possibly particles of longer range. Mäder, indeed, definitely reports the existence of a group of protons of range 1·37 cm., but so far this result has not been confirmed by other observers.

The tracks of the particles have therefore been obtained on a photographic plate, by soaking the plate in a solution of samarium sulphate. Since the solubility is low the concentration is small, and long exposures, of the order of a month, are required in order to obtain a large number of tracks. The plate on which the measurements have been made shows about 25,000 tracks per cm^2, but for reasons already given, very few of these are suitable for measurement. For increased accuracy, we have restricted ourselves to tracks which are almost exactly horizontal. The number of measurements in the group is 310.

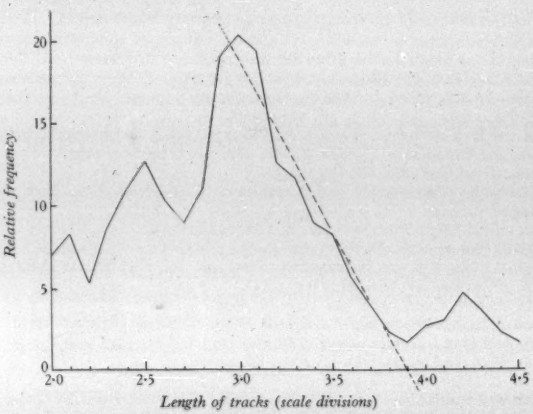

Figure 6. Distribution curve of the tracks produced by the α particles of samarium. The peak on the extreme right represents the beginning of the distribution curve of the longer tracks.

The distribution curve is shown in figure 6. It is apparent that by far the great majority of the tracks can be ascribed to the short-range α particles. We can determine the extrapolated length in the usual way, and calculate the range in air. The probable error in the determination will be the same as for the boron-disintegration tracks, since the number of observations and the actual range are approximately the same for both. We find the value

$$R = 1{\cdot}13 \pm 0{\cdot}02 \text{ cm.}$$

This value is in agreement with previous determinations, but is appreciably more accurate.

It is evident from the measurements that there are particles present of much greater range. The measurements are not inconsistent with the existence of the group of protons reported by Mäder, but do not definitely confirm it. It is manifest, however, that particles of range up to about 3·5 cm. in air are present, and for reasons

already outlined[19] we are strongly of the view that these are singly-charged particles and not α particles. We hope to give a fuller account of these long-range particles at a later date.

§ 10. ACKNOWLEDGMENTS

It is a pleasure to express our thanks to the research staff of Messrs Ilford, Ltd., for their cooperation in the production of *R* plates; to our colleagues in the Chemistry Department of the Wilson College for help in the preparation of solutions; and to Professor J. Chadwick, now of Liverpool University, and Professor Lord Rutherford, of the Cavendish Laboratory, for their continued interest and encouragement.

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THE DETERMINATION OF THE VISCOSITY OF LIQUID GALLIUM OVER AN EXTENDED RANGE OF TEMPERATURE

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ABSTRACT. On theoretical grounds measurements of the viscosities of liquids over as wide a temperature-range as possible are desired. Gallium is particularly suited for this purpose, and the viscosity of the molten metal has been measured between its melting point (approximately 30° C.) and 1100° C. This is a much wider range of temperature than has hitherto been recorded in viscosity-measurements. It has been necessary to devise a special technique on account of practical difficulties connected with surface films. At 1100° C. the viscosity decreases by only 2 per cent per 100°.

§ 1. INTRODUCTION

Recent theoretical work on the subject of liquid viscosity by Prof. E. N. da C. Andrade[1] has made it specially desirable that the viscosity data for elementary substances should be augmented. In this connexion the liquid metals form an important group, but, except in the case of mercury, reliable viscosity-measurements have been made in a few cases only, and even in these cases the temperature-range is comparatively restricted. The work described here was undertaken with the object of investigating the viscosity of an elementary substance over as wide a range of temperature as possible. Gallium was chosen for these experiments on account of its low melting-point (30° C.) and high boiling point (unknown, but certainly above 1600° C.), which make it exceptionally suitable for the purposes of the present research. Actually, with the technique developed, it has been found possible to measure the viscosity of liquid gallium between its melting-point and 1100° C.

The first question which arose was that of choosing a method suitable for viscosity-determinations with a substance of which, owing to its high cost, only 2 or 3 cm^3 were available. Of the variety of methods which have been developed for measuring viscosities, only the capillary-tube method seemed feasible with such quantities. This method was, therefore, adopted, in spite of unexpected difficulties encountered in the manipulation of the liquid gallium as a result of the existence of an obstinate surface film. To overcome this film a special technique was worked out, an account of which is given below.

Before proceeding to the description of the experimental work, it may be mentioned that the validity of the assumption that there is no slip at a solid boundary

during laminar flow has been questioned from time to time in the case of mercury. This question has an important bearing on the present experiment, since the behaviour of gallium, after the treatment described in this paper, is very similar to that of mercury. In a critical summary of the situation, however, S. Erk[2] has come to the conclusion that there is no valid evidence for the existence of slip in the case of mercury, the arguments in favour of its existence being based upon experiments where other effects, such as turbulence, or corrosion of the material of the capillary tube, have produced disturbing results.

The gallium used in this investigation was not spectroscopically pure, but while minute quantities of impurities have a marked effect on such properties as surface tension and on the mechanical properties of a metal in the solid state, their effect on liquid viscosity is relatively very small. The impurities were estimated not to exceed 0·1 per cent.

§ 2. PRELIMINARY EXPERIMENTS

In the preliminary experiments it was found that liquid gallium wetted both glass and quartz when manipulated in the presence of the atmosphere. Thus, when placed in a viscometer, it presented no definite meniscus on which observations could be made, and it stuck fast in the narrow capillary tube. Immediately it became evident that the simple procedure normally followed in determinations with the Ostwald viscometer would have to be modified considerably. Before any viscosity measurements could be made, therefore, the gallium had to be obtained in a state in which the essential conditions for the determination of liquid viscosities by the capillary-tube method were satisfied, namely (i) that the liquid shall flow freely without interruption under the smallest pressure-difference, and (ii) that it shall present a definite meniscus on which measurements of the rate of flow can be made.

It was found that gallium no longer adhered to the glass when there was a little dilute hydrochloric acid present. The sticking first observed, therefore, was thought to be due to a surface film of oxide. Although the action of the dilute acid on the gallium was very slow, it was quite sufficient to counteract the effect of the atmosphere, and the metal in contact with the acid behaved like a clean globule of mercury.

The next step was to get the gallium to behave similarly without the presence of the acid. This was done by placing some gallium, together with a little dilute hydrochloric acid, in a glass container and evacuating through suitable traps. The gallium showed no tendency to adhere to the glass, even after the last trace of acid had been eliminated. Thus it was obtained *in vacuo* in what will henceforth be referred to as the *flowing state*. As soon as air was readmitted, however, the gallium began to adhere to the walls of its container, as it had done in the first instance.

It was now desirable to find, if possible, some gas having no effect upon gallium, since the usual method of resetting a capillary viscometer is to restore the differences of head by means of gas pressure. With this object in view various gases, both

neutral and reducing—nitrogen, carbon dioxide, hydrogen and argon—from which traces of oxygen had been carefully removed, were tried. No gas could be found, however, in which the behaviour of the gallium was satisfactory. It was decided, therefore, to design a viscometer in which measurements could be made *in vacuo*.

As a precaution against contamination, the above tests were carried out with a few grammes separated from the main stock of gallium.

§ 3. FIRST APPARATUS

The apparatus which was made for the purpose of finding out if the vacuum method was practicable is shown in figure 1, and was made of soft glass. It is drawn approximately to scale, the actual height of the apparatus being about 27 cm. Gallium was first of all placed in the reservoir *C* with a little dilute acid. On evacuation the acid evaporated, leaving the metal in the flowing state. It was then introduced into the flow-tube part of the apparatus through the side tube to the left of *C*, and made to flow round to the other side through a fine capillary tube *D* of internal diameter 0·04 cm. The viscometer was clamped to a suitable

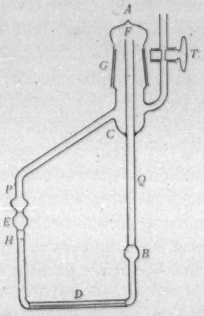

Figure 1.

holder at the points *P* and *Q* and mounted in a thermostat. The mounting of the viscometer allowed it to be tilted so that the gallium flowed into the bulb above *E* on the left-hand side. To take a reading, the viscometer was turned back to an upright position, and the meniscus was timed between the marks at the top and bottom respectively of the bulb *E*. The amount of gallium was adjusted to extend between the mark *H* and the mark at the top of bulb *B* on the right-hand side. The provision of a cover *A*, adapted to the apparatus by means of the ground joint *G*, facilitated the operations of the cleaning, filling and emptying and the extension of the tube *F* above the top of *G* helped further in this direction.

Readings were obtained between 30° C. and 50° C., and the results are shown in table 1. The apparatus was calibrated with pure benzene. It would, of course, have been better to carry out the calibrations with mercury since this liquid more

Table 1. Preliminary measurements of the viscosity of gallium

Substance	Temperature (°C.)	Time (sec.)	Density ρ	η/ρ (Stokes)	Viscosity η (poise)
Benzene	30·5	585·6	0·8675	—	0·00560
Mercury	30·5	105·3	13·52	—	0·0150
Gallium	30·5	295·0	6·095	0·003231	0·01969
	30·5	292·0	6·095	0·003200	0·01950
	35·0	288·2	6·091	0·003158	0·01924
	40·0	282·1	6·088	0·003087	0·01879
	50·0	269·9	6·080	0·002984	0·01814

nearly resembles gallium in its properties than benzene does; but the kinetic-energy correction to be applied to readings obtained with mercury was too large for that liquid to be used otherwise than for the purpose of obtaining an approximate value of a corresponding, but smaller, correction to be applied to the gallium readings. In the case of the final apparatus, however, it was found possible to use mercury for the whole of the calibration. Since the melting-point of gallium is somewhat above room-temperature, precautions had to be taken against its solidification in the viscometer. The substance could often be super-cooled considerably, but it could never be relied upon to remain in the liquid state indefinitely when it was at a temperature below the melting-point, and solidification would probably have broken the apparatus since gallium expands appreciably in the process. The density in the liquid state at the melting point is 6·095 g./cm.^{3}, while in the solid state at the same temperature the density falls to 5·904 g./cm.^{3} [3].

The experience gained with this preliminary apparatus was sufficient to prove the feasibility of the vacuum method, and it was decided to employ similar principles in the design of a quartz viscometer for use in an electric furnace at high temperatures. Before designing such an apparatus it was necessary to know something of the probable behaviour of gallium at high temperatures, and particularly of the effect of the chloride which must have been present after the metal had undergone the treatment described above.

A paper by Sylvester Boyer [4] on the use of gallium in a high-temperature thermometer gives valuable information on the manipulation of gallium at high temperatures, and confirms one or two observations made by the writer before he was aware of Boyer's work.

Boyer, like the writer, experienced trouble due to the wetting of quartz and glass by gallium, and attributed it to surface oxidation. In the technique he evolved to overcome this, Boyer also made use of the reaction between the surface oxides of gallium and dilute hydrochloric acid to prevent oxidation during the evacuation of his apparatus. When the gallium was heated the chloride was found to volatilize, leaving the metal brighter than before and showing no signs of wetting its container. Boyer alludes to two chlorides with boiling-points one at about 210° C. and the other at 535° C.

This volatilization of the chlorides on heating was verified by the author of the present paper. The gallium was treated with dilute hydrochloric acid in an evacuated

quartz glass container and heated. A thin grey deposit, evidently chloride, was formed on parts of the container which were not directly heated, while the surface of the gallium became somewhat brighter. A consideration in the design of a viscometer for use with gallium at high temperatures was, therefore, the prevention of contamination of important parts of the apparatus by the chloride evolved during the preliminary treatment.

§ 4. DESIGN OF AN APPARATUS FOR HIGH-TEMPERATURE MEASUREMENTS

The following considerations had to be borne in mind. (i) The gallium was to be kept *in vacuo*, and therefore, the setting of the apparatus must be by tilting. Owing to the success obtained with the preliminary apparatus, it was, in fact, desirable to follow the principles used in its design as closely as possible. (ii) For satisfactory uniformity of temperature the internal diameter of the furnace to be used for the high-temperature measurements must be fairly small in comparison with its length. Therefore the viscometer must be designed to fit inside a tube only a few inches in diameter. (iii) The apparatus must be reasonably easy to clean, fill and empty. (iv) It was desirable, for simplicity, to carry out the pretreatment of the gallium and the measurements in the same unit.

Two methods of determining the time of flow of the gallium in the viscometer were available. Either the flow could be observed directly by eye or, since gallium is a good conductor of electricity, the rate of flow could be determined by movement with respect to a system of electrical contacts in fixed positions inside the viscometer. The chief objections to the electrical contact method were as follows. (i) The difficulty of sealing a metal wire into quartz glass (which would, of course, have to be the material used for the construction of the viscometer) and of making the resultant seal vacuum-tight over an extended range of temperature. (ii) The possible contamination of the gallium and of the mercury used in the calibration by the metal used for the contact wires, and of the wires themselves by the liquids used in cleaning the apparatus; and finally (iii) the impossibility of observing whether any tailing takes place at the contacts as the gallium meniscus traverses them.

On the other hand, the method of direct observation possesses obvious advantages, both as regards accuracy and convenience. The only difficulty was to arrange suitable windows in the furnace for illumination and observation.

It was, of course, realized that the method of time-measurement employed in many investigations on liquid viscosities at high temperatures was one using electrical contacts (see e.g. F. Sauerwald[5], Sauerwald and Toepler[6], and Goodwin and Mailey[7]), but in all these cases it was possible to design the viscometer in such a way that the part carrying the contacts could be removed as a separate unit. In the present case, however, the form of the apparatus was restricted on account of gas pressure not being available for resetting, and it was, therefore, not possible to arrange for such a simplification.

The quartz apparatus described below is, so far as is known to the writer, after

examination of the literature, the only viscometer which has been designed for use at high temperatures where the flow may be observed directly, and where the presence of gas in contact with the substance under investigation is dispensed with.* It has been found quite satisfactory in use at temperatures above 1000° C., and might possibly be used, with minor alterations, for measurements with other substances.

§ 5. DESCRIPTION OF THE APPARATUS AND THE METHOD OF USING IT

The apparatus which satisfied all the conditions laid down above is drawn to scale in figure 2. It was about 47 cm. in length and was made to fit, with a small clearance, inside an electric furnace, the tube of which was about 7·5 cm. in diameter and about 42 cm. in length. The actual viscometer was contained in the rectangle *ELIN*; thus, when the viscometer was in position inside the furnace the long tube *B* projected outside, and the joints *C* and *D* and the tap *T*, at the end of *B*, remained quite cool and could be sealed with vacuum grease in the usual way. The material of the covers *F* and *G*, fitting on to *C* and *D* respectively, was, therefore, pyrex glass instead of quartz glass. *F* was only to give access to the tube *A* during cleaning, while *G* carried the tap *T* through which the viscometer was evacuated,

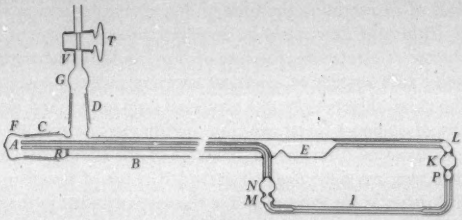

Figure 2.

and provided a more convenient opening for the introduction of the gallium. As a precaution against breakage the long inner tube *A* was supported near its end by a small pillar *R*.

To fill the viscometer, a suitable amount of gallium was placed in the small reservoir *E* and treated with hydrochloric acid in order that it might be in the flowing state *in vacuo*. This was done at room-temperature. The viscometer was then adjusted inside the furnace in the position it was to occupy when the measurements were being made, the gallium being in the reservoir *E*. The clamp supporting the viscometer held the tube *B* at a point outside the furnace and was fixed to a rail-and-slider arrangement allowing easy movement of the apparatus in and out of the furnace tube. The temperature of the furnace was allowed to rise until it

* Recently a reference has appeared (*Science Abstracts*, January, 1935) to work carried out by S. Dobiński[8] on the viscosity of liquid phosphorus *in vacuo* with an Ostwald viscometer between the temperatures 17·5 and 80° C. A copy of the paper is not yet available to the writer.

was above 600° and it was then kept steady for about 2 hours. This treatment drove off the chloride from the gallium, together with any dissolved gas which might have been present. Pumping through the tap T was kept up all the time with a Hyvac pump. The first sign of deposition of gallium chloride was always observed on the inside of the tube B, just where it emerged from the furnace, at a place where the temperature was a little below 250° C. Chloride was deposited on the cool parts only of the apparatus, and thus the essential parts, including the bulbs and capillary tube which were inside the furnace, were not contaminated. At the end of 2 hours the furnace was allowed to cool down to about 200° C., at which temperature the filling of the viscometer could be carried out comfortably. To fill the viscometer, the gallium was allowed slowly to approach the entrance of a fine capillary I of diameter 0·04 cm. It was made to flow through I by inclining the viscometer slightly and tapping it gently with a wooden ruler. This was the most difficult operation in these experiments. Great care had to be observed in preventing the gallium from breaking up into small threads which, like those of mercury, stick fast in a fine capillary tube. Any possibility of solidification of the gallium during the filling operations was eliminated by holding the viscometer with its end projecting into the furnace tube.

After filling, the viscometer was adjusted inside the furnace tube so that the capillary I occupied a central position. The essential parts of the viscometer, occupying a length of about 17·5 cm., were thus in a position where the temperature was uniform. Actually the largest temperature-difference observed between the ends of the viscometer at high temperatures was 2° C. To adjust the viscometer in a vertical plane, it was aligned with a plumb line from the end-on position, and its inclination could be reproduced by means of a fixed optical-lever system used in conjunction with the small galvanometer mirror cemented to the apparatus at V.

The furnace tube was closed in by means of close-fitting asbestos ends. These both contained small double mica windows to allow observation of the viscometer inside. Windows were provided at both ends in order that a beam of illumination might be projected through the tube of the furnace.

To make a measurement, the furnace was adjusted to the required temperature and a cathetometer was arranged so that the bulb K of the viscometer could be observed. The viscometer was set for a reading by tilting the furnace so that the gallium meniscus rose above the mark at the top of the bulb K. The clamp holding the viscometer was, of course, connected to the outside of the furnace, so that any movement of the furnace was shared by the viscometer. In order that the tilting might be carried out conveniently the furnace, which was of the usual box type, was mounted on trunnions. As soon as sufficient gallium had flowed into the right-hand limb of the viscometer the furnace was tipped back to its former position and secured by stops attached to the trunnions, and the passage of the gallium between the marks at the top and bottom respectively of the bulb K was timed with a stop watch in the familiar way.

This process could be repeated as often as desired. Usually five readings of the time of transpiration were taken at each temperature.

It is worth mentioning that since the marks themselves were rather difficult to keep in view it was found much more convenient to adjust the cathetometer cross-wires to the marks at leisure, and then to time the meniscus past the cross wires.

A small pocket L above the bulb K was provided in order that the meniscus might not pass the mark too soon to be observable, while a margin bulb M was made below the bulb N to obviate the risk of the gallium all flowing into the right-hand side of the viscometer during setting.

Thermocouples were used for the measurement of the temperatures. An iron-constantan couple was used between 150° and 600° C., while above 600° C. a platino-rhodium couple was used. The thermo-electric e.m.fs. were measured with a Crompton potentiometer. Calibrations were made at the melting points of suitable metals, and were repeated from time to time during the course of the work. No change was detected, however. The possible error in the measurements with the iron-constantan couple was between 1° and 2° C. In the case of the platinum-platinum-rhodium couple the possible error was about 3° C., the error being larger on account of the smaller thermo-electric e.m.f. In both cases the error introduced into the viscosity measurements is negligible.

At temperatures above 800° C. mica is not a suitable material for the observation windows, and quartz glass was substituted. The joints C and D and the tap T always remained quite cool, whatever the furnace-temperature. As a special precaution against contamination of the gallium, however, apiezon grease, which is known to have an extremely low vapour-pressure, was used on the joints in place of ordinary vacuum grease during the measurements at 800° C. and above.

§ 6. CALIBRATION

The calibration of the viscometer was carried out with mercury. It was not possible to choose the dimensions of the apparatus in such a way that the kinetic-energy (sometimes referred to as the Hagenbach-Couette) correction could be neglected, so it was determined directly by experiment. This seems to be the most satisfactory method of applying the correction in view of the fact that there is still some uncertainty about its magnitude, even in the case of viscometers in which the ends of the capillary are submerged in the liquid.

η The equation* for the determination of the viscosity η of a liquid with a viscometer of this type is

$$\eta = A'\rho T - B\frac{\rho}{T},$$

T, ρ A', B where T is the time of transpiration of the liquid in the viscometer, ρ its density, and A' and B are constants for the instrument. The term $B\rho/T$ is the kinetic-energy correction term. Calibration consisted, therefore, in the determination of the constants A' and B, the viscosity of the gallium at any temperature being then calculable from a knowledge of its density and time of transpiration.

To determine A' and B, the time of transpiration for mercury was obtained at

* See, for instance, Barr[9] whose notation is adopted here.

various temperatures. B could then be found from the slope of the graph of $\eta/\rho T$ against $1/T^2$, the values of η and ρ being known from the International Critical Tables. The value of A' was obtained by dividing $\eta/\rho + \beta/T$ by the corresponding value of T at each temperature, and taking the mean.

Calibrations were carried out for two positions of the viscometer since, for some of the readings with gallium, it was found better to increase the rate of passage of the meniscus past the marks by inclining the apparatus slightly. The values of B obtained at the two inclinations used are seen to be practically the same, table 2, as they should be, since B contains terms depending only on the dimensions of the

Table 2. Calibration of the quartz viscometer with mercury

Temperature (°C.)	Time (sec.) inclination 0°	Time (sec.) inclination 5°	η/ρ (Stokes)
15	110·6	67·2	0·0011655
50	100·0	61·4	0·0010370
100	89·2	55·3	0·0009060
200	78·0	49·0	0·0007700

$A' = 1{\cdot}118 \times 10^{-5}$, $B = 0{\cdot}00800$ } inclination 0°

$A' = 1{\cdot}915 \times 10^{-5}$, $B = 0{\cdot}00833$ } inclination 5°

viscometer. The slight difference observed is due to the fact that B, having its origin in a small correction, is not determinable with a high degree of accuracy. Nevertheless, since the maximum kinetic-energy correction applied was only about 10 per cent, and in most cases the correction was much smaller, the actual uncertainty introduced is negligible. The mutual consistency of the values obtained for the constant A' was better than 1 part in 200, but the real accuracy naturally depends upon the precision with which the viscosity of mercury is known.

During the calibration a few readings had to be taken with slightly different quantities of mercury. This was done for the purpose of applying a small correction necessitated by the fact that the quantity of gallium could not always be adjusted exactly to fill the space in the viscometer between the mark P on the right-hand side and the mark at the top of the bulb N on the left.

Since such a big range of temperature was used in these experiments, it seemed possible that there might be a correction owing to expansion of the bulbs and capillary tube of the viscometer. When calculated, however, the magnitude of this correction was found to be only 1 part in 2000.

§7. DISCUSSION OF RESULTS

The results obtained for the viscosity of liquid gallium up to 1100° C. are given in table 3 and are shown plotted in figure 3. These readings were obtained with different fillings of gallium over a period of about 3 months. At a few places results are shown repeated at nearly the same temperature (e.g. 97·7° and 102°, and 200° and 203°); they were taken with different fillings, and indicate the consistency with which the

Table 3. Viscosity of gallium

Temperature (°C.)	Time (sec.)	η/ρ (Stokes)	Density ρ	Viscosity η (poise)
[30]	—	—	—	0·02037
52·9	165·2	0·003115	6·080	0·01894
97·7	142·3	0·002668	6·042	0·01612
102	141·7	0·002656	6·041	0·01604
149	125·7	0·002341	6·005	0·01406
200	193·1*	0·002120	5·972	0·01266
203	112·5	0·002082	5·970	0·01243
301	95·5	0·001743	5·905	0·01029
402	139·6*	0·001504	5·840	0·008783
402	84·3	0·001517	5·840	0·008858
500	78·7	0·001404	5·779	0·008113
500	131·5*	0·001409	5·779	0·008141
600	126·0*	0·001345	5·720	0·007694
600	75·9	0·001347	5·720	0·007705
604	123·0*	0·001310	5·718	0·007491
806	67·1	0·001164	5·604	0·006524
1010	103·3*	0·001077	5·492	0·005915
1100	62·3	0·001062	5·445	0·005783

* Readings taken with viscometer-inclination of 0°. All the rest were taken with an inclination of 5°.

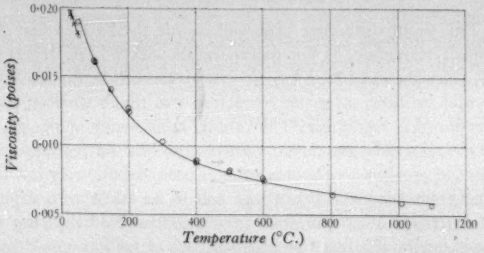

Figure 3.

results could be repeated. Pairs of results (e.g. at 500°) were taken with the same fillings to check the consistency between results obtained at the different inclinations used. The agreement is seen to be quite good.

The few results obtained with the preliminary apparatus, table 1, are shown plotted as crosses on the same graph. It will be seen that these are about 4 per cent lower than those obtained with the final quartz apparatus. This, however, is not very surprising when the differences between the two methods are remembered, as well as the fact that the calibrations were made with such different liquids as benzene and mercury. Little weight, then, is to be attached to the absolute values obtained in the preliminary experiments, but they are given here because it is worth noting that the rate of change of viscosity obtained with the first apparatus is consistent with the final measurements.

Measurements obtained with a viscometer only give the values of the kinematic viscosity η/ρ directly; therefore the value of the density of the liquid investigated must be known before the actual viscosity in poises can be calculated. The only value for the density of liquid gallium given in the literature[3] is for a temperature near its melting-point, but experiments have been made in this laboratory by W. H. Hoather to determine the density of gallium over a wide range of temperature, and my thanks are due to him for allowing me to use some of his results before publication.

The value of the viscosity of gallium at the melting-point is 0·0204 poise. This is of the same order as the value, namely 0·0146 poise, predicted from the formula

$$\eta_m = 5{\cdot}1 \times 10^{-4} \frac{(AT_m)^{\frac{1}{2}}}{V_A^{\frac{2}{3}}},$$

given by Andrade's theory, η_m being the viscosity of an elementary substance at its melting-point, T_m the absolute temperature of the melting point, A the atomic weight, and V_A the atomic volume.

Andrade's theory contemplates a close-packed cubic structure, and the agreement with experiment is close for metals possessing such a structure, while for structures which are not close-packed the value given by the formula is too small. Thus gallium, which has a complicated crystalline structure (orthorhombic with distorted close-packing) behaves as was to be expected in having a melting-point viscosity of the order of, but somewhat in excess of, that predicted.

In part II of his paper on the theory of viscosity[1] Andrade has advanced a formula to give the variation of the viscosity of a liquid with temperature. This formula is

$$\eta v^{\frac{1}{3}} = Ae^{\frac{c}{vT}} \qquad \text{.....(1),}$$

where v is the specific volume of the liquid at the absolute temperature T, and A and c are constants. Values of A and c have been chosen by the method of least squares, applied as described in Andrade's paper, to give the best fit between equation (1) and the experimental results. This is the largest range of temperature over which the formula has yet been fitted, and it is satisfactory to note that the agreement is reasonably good, the maximum deviation being 3·9 per cent. A comparison between the experimental values and the calculated values of the viscosity of liquid gallium at different temperatures over the whole range may be made by referring to table 4, and to figure 3, where the curve shown represents the theoretical formula with the constants found as above. It is seen from the results that the viscosity of gallium only drops to about one third of its value over a range of more than 1000° C. and, correspondingly, that the value of the constant c in equation (1) is very small compared with the values for most other liquids, excepting mercury. This slow variation of viscosity with temperature in the case of a substance with a monatomic molecule agrees well with the views put forward by Andrade.* It may be noted that at the highest temperature, 1050° C., the viscosity diminishes by only 2·3 per cent for a rise of 100° C.

A

c

* See reference (1), part II, page 724.

Table 4. Comparison with experimental results of theoretical values, calculated from equation (1). Range of η, 3·3. $A \times 10^8 = 246800$; $c = 79{\cdot}05$

Temperature (°C.)	η observed	η calculated	$\frac{\eta_{calc.} - \eta_{obs.}}{\eta_{obs.}} \times 100$
52·9	0·01894	0·01968	+3·91
100	0·01608	0·01617	+0·56
149	0·01406	0·01382	−1·71
200	0·01258	0·01215	−3·42
301	0·01029	0·01006	−2·24
402	0·008820	0·008807	−0·15
500	0·008127	0·007997	−1·60
600	0·007637	0·007409	−2·98
806	0·006524	0·006608	+1·28
1010	0·005915	0·006107	+3·34
1100	0·005783	0·005940	+2·71

The highest temperature at which measurements were made in this work has been exceeded by other investigators in determining the viscosities of molten metals, for instance by Thielmann and Wimmer[10] for iron with 2·5 per cent of carbon at 1400° C., and by Bienias and Sauerwald[11] for copper; but on account of the fairly high melting-points of most metals the ranges of temperature used have been small, not more than about 450° C. at the most. The most extensive measurements on metals, except in the case of mercury, which appear to have been made up to the present are on lead by Bienias and Sauerwald[11] between 441° and 844° C., and on tin by Pluss[12] and by Sauerwald and Toepler[6], between 280° and 750° C. So far as is known, therefore, the measurements described in this paper are the only ones which have been made on a single substance over anything like such a large range of temperature.

§8. ACKNOWLEDGMENTS

In conclusion, I should like to express my thanks to Prof. E. N. da C. Andrade for introducing me to this work, for the many valuable suggestions which he has made, and for the great interest he has shown throughout its course. My thanks are due also to the Department of Scientific and Industrial Research for a grant extending over part of the period during which it was being done.

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DISCUSSION

Mr C. R. DARLING suggested that the author should make measurements on tin, which remains liquid over a wide range of temperature and keeps a clean surface.

532.612.4

THE RIPPLE METHOD OF MEASURING SURFACE TENSION*

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ABSTRACT. An apparatus for the production, stroboscopic observation, and measurement of ripples for surface-tension determinations is described. The principal features are the use of a mirror attached to a vibrating reed as the means of obtaining intermittent illumination and a valve oscillator for actuating the dipper. Frequencies are measured by causing the oscillator to light an Osglim lamp which illuminates a stroboscopic disc attached to a phonic motor running at a constant speed.

The dynamic quality of the ripple method is discussed and it is shown that the local change of area of the surface due to the passage of ripples would be expected to be negligible.

Measurements of the fall of surface tension of a slowly adsorbed solution show that the method gives results similar to those obtained by a truly static method and it is concluded that the ripples have no retarding effect on the attainment of surface equilibrium.

§ 1. INTRODUCTION

The equation for the propagation of surface waves under the combined influence of gravity and surface tension was put forward by Kelvin[1] as

$$v^2 = \frac{g\lambda}{2\pi} + \frac{2\pi T}{\lambda\rho},$$

v, g subject to certain conditions, where v is the velocity, g the acceleration due to
λ, T, ρ gravity, λ the wave-length, T the surface tension, and ρ the density.

This equation provides the theoretical basis of a method of determining surface tension involving the measurement of wave-lengths and frequency. Such an experiment is rather more cumbersome than some of the commoner methods, and since the expression giving T involves the cube of the wave-length, considerable accuracy of measurement is required. It has the advantage, however, of resting on a surer theoretical foundation than some of the methods in general use, and also of being independent of contact angle.

A number of authors have worked with the ripple method and a fairly comprehensive bibliography is to be found at the end of this paper.

§ 2 DISCUSSION OF POSSIBLE TECHNIQUES

If the production and measurement of ripples are undertaken with a view to determining surface tensions, the procedures which may be adopted are as follows.

* The substance of this paper formed part of a thesis submitted for the degree of Ph.D. to the University of London.

(*a*) *Photographic.* Progressive waves are produced by a single point-, or line-source, and instantaneous photographs are taken, the time of exposure being made as short as possible. The negatives may then be measured and reductions made in order to arrive at the actual wave-lengths. Vincent[11, 12] made use of spark photography with considerable success.

(*b*) *Stationary waves.* Two synchronous sources of disturbance are used in such a way that standing waves occur on the liquid surface. Wave-lengths are then measured by means of a travelling microscope or cathetometer arranged above the tank. Authors who have described experiments involving stationary waves are Michie Smith[13], Matthiessen[2,3], Grunmach[14], Kalähne[9], and Beckett and Sheard[15].

(*c*) *Stroboscopic.* In this method progressive waves are made to appear stationary by viewing them in intermittent light of the same frequency as the waves. It follows that the sharpness of the lines or images so observed will be improved by arranging that the duration of the flash shall be as short as possible. Methods of providing the stroboscopic illumination are numerous and may be classified as follows: (i) Light metal shutters having slits cut in them may be attached to the prongs of an electrically maintained tuning-fork. If they are so arranged that light passes through both of them when the fork is at rest, two flashes are produced for each vibration of the fork. References for this technique are: Rayleigh[4], Dorsey[6], Barnett[16], and Watson[8]. Hartridge and Peters[17] produced their ripples by means of a mechanical vibrator driven by a motor which also turned a slotted disc. This provided the interrupted illumination. Tyler[18] has used a.-c. mains to actuate both his dipper and a phonic motor carrying a slotted disc. (ii) Some authors have caused the current which drives the dipper also to operate a glow-discharge lamp of the Osglim type, a stroboscopic effect being thus obtained. Such experiments were carried out by Pfund[19] (who produced the ripples by an electrostatic method), Thatte and Nilkanthan[20], and Tyler[18]. (iii) Another procedure which suggests itself is the use of a Kerr cell in conjunction with polarized light after the manner of television experiments. (iv) A small mirror attached to a vibrating reed may be used as a source of interrupted light if the reflected beam is caused to pass through a slit at one stage of its vibration.

As far as can be ascertained methods (iii) and (iv) have not hitherto been used in connexion with ripples.

§ 3. TECHNIQUE AND APPARATUS ADOPTED

(i) *Production of waves.* In the present investigation a glass plate or style D, figure 1, was attached to the free end of a horizontal strip of iron R_1 which was clamped between metal plates at some point along its length. The natural frequency of this vibrator could then be varied by clamping at different points. Above it was held the magnet of a loud-speaker unit U_1 at such a distance as to give the required amplitude of the vibration of the reed for a given current in the energizing coils. This current was derived from a valve oscillator consisting of a single L.S. 5 valve

connected with inductances and capacities in the usual way. By a suitable choice of values for these the frequency of the a.-c. output could be varied over a wide range and adjusted finely by means of a variable condenser. For any chosen frequency the length of the vibrator was so adjusted that its natural frequency was the same as that of the output of the valve oscillator.

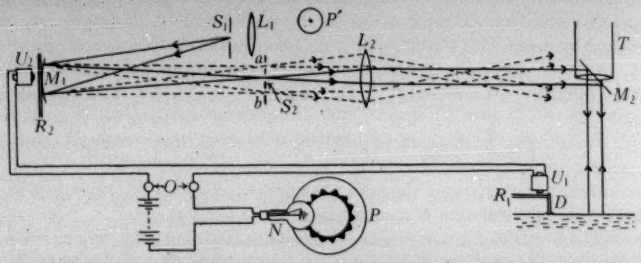

Figure 1. Diagram of ripple apparatus.

(ii) *Checking and determination of frequency.* The output of the oscillator O was connected to a small Osglim lamp N in series with a dry h.-t. battery whose voltage was adjusted so as to be just too small for the striking of the lamp. Thus the lamp gave one flash for every complete cycle of the a.-c. The lamp was made to illuminate a stroboscopic disc P mounted on the spindle of a phonic motor which was at first driven by a standard electric tuning-fork of frequency 50 and later by the a.-c. mains, which had a controlled frequency of the same value. By means of different rings containing various numbers of spots or triangles on the stroboscopic disc the oscillator could be set to produce many different frequencies, and when necessary these could be adjusted very finely so as to be perfectly reproducible. The frequency of the electric tuning-fork used initially was determined accurately by allowing it to drive the phonic wheel and noting, by means of a counter, the number of revolutions of this in a number of hours registered by a reliable chronometer. Thus, with only one standard available, waves of many different known frequencies could be used.

(iii) *Optical arrangements.* Since in previously published work the method of observing and measuring ripples with the help of intermittent light seemed to have led to greater precision than other methods this technique was adopted in the present work.

After careful consideration of all the methods enumerated in § 2(*c*) and after testing all except that in which the Kerr cell is used, the author decided to use the vibrating mirror. No previous record of its use in this connexion has been found. In fact, as a source of intermittent light which can very easily be set up its possibilities do not seem to have been explored at all thoroughly.

A reed R_2 similar to that carrying the dipper was clamped in an upright position, and a concave galvanometer mirror M_1 of radius 1 metre was attached to its face

near the free end. The permanent magnet and coils of a loud-speaker unit U_2 were clamped near to the reed on the opposite side to that to which the mirror was attached. The whole was mounted firmly on a levelling-table supported on three levelling-screws and provided with a vertical motion. U_1 and U_2 were connected in series with the oscillator output.

Light from a Pointolite lamp P' passed through a horizontal slit. A real image of the slit was formed at the position S_2 where another slit was placed, but the latter was afterwards found to be unnecessary. From here the light passed on through a cylindrical lens L_2, placed in such a position that S_2L_2 was equal to the focal length of L_2, and thence on to the plane mirror M_2 which was attached to the telescope T of the cathetometer. Thus the light passed from M_2 down on to the liquid surface and was then reflected nearly normally up the telescope. M_2 did not obstruct the telescope objective since it was situated alongside it, and therefore the rays incident on and reflected from the liquid surface were not quite normal to it. Adjustments of M_1, M_2 and T were made so that when M_1 was at rest a patch of light was seen in the field of the telescope. If then the a.-c. was applied to the coils behind M_1, the image formed at S_2 was spread out into a band *ab*, and if S_2L_2 was less than S_2M_1 the angle between the extreme rays was increased by the introduction of the lens L_2. Light reached an eye, which was looking down the telescope, twice for each vibration of M_1 and consequently, if the surface of the liquid was carrying ripples, stationary lines were seen in the field, and the distance between two alternate lines was a wave-length. The apparatus will work for any frequency provided the reeds R_1 and R_2 are made to respond to that frequency by alteration of their lengths. Apart from this and the extreme simplicity of the arrangement there is another important point in its favour. Clearly the sharpness of the lines produced by any system of stroboscopic illumination is increased if the fraction of the cycle during which the flash is made is reduced. At first L_2 was not included in the arrangement and the sharpness of the lines was improved by increasing the amplitude of the mirror M_1 and placing a narrow slit at S_2. There is a limit to the amplitude, however; moreover it was found that the slit S_2 was not effective unless it was made so narrow that the intensity of the illumination began to suffer. In other words, the limitation of the duration of illumination was being governed by the optical properties of the telescope rather than by the slit S_2. Accordingly S_2 was dispensed with and the introduction of L_2 had the desired effect.

It seems that this is the most suitable method of producing intermittent illumination of any frequency in which the fraction of the cycle during which illumination takes place is adjustable down to extremely small values. The alternative methods previously mentioned have not this advantage unless more complicated arrangements are added to them, such as inductances and condensers to modify the wave-form in the case of the Osglim lamp.

(iv) *The tank.* This was very kindly lent by Dr N. K. Adam, F.R.S., and was of the standard form used by him in surface-film experiments. After being thoroughly cleaned the inside of the tank was coated with a thin layer of wax. When in use the

tank rested on two pads of sponge rubber each 2 in. thick and placed on a concrete floor. With this arrangement vibrations were not troublesome. Small gas burners were inserted under the tank between the pads.

Waxed glass strips were used to sweep the liquid surface. The fact that these can be used to renew the surface so effectively may be recorded as one of the advantages of the method of ripples.

§ 4. OPERATION

On switching on the oscillator and setting its frequency at the predetermined value by means of the Osglim lamp and steadily rotating phonic wheel, lines parallel to the dipper could be seen in the telescope. These were focal lines formed by the reflection of parallel light by the concave or convex surfaces comprising the troughs and crests of the waves respectively. Thus for a given position of the telescope along the horizontal scale it was possible to obtain sharp images at two different focusings, one above and one below the liquid surface. As the line of sight of the telescope was moved away from the dipper, the two sets of images separated more and more since the amplitude and, therefore, the curvature of the waves decreased. Figure 2 is a photograph of the lines obtained when water was used, the frequency being 300 c./sec. and the wave-length 0·172 cm. An exposure of 1 minute was

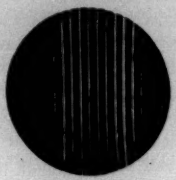

Figure 2.

necessary even with the ultra-fast plate; consequently some of the sharpness is lost owing to slight surface movements. It will be noted that maximum sharpness is shown by the central images which are produced by reflection from the troughs. In the formation of the other lines the sloping parts of the wave-outline are involved. A convenient point to work at was approximately midway between the dipper and the region where the images become indistinct. Here the telescope could be set on a series of perhaps half a dozen waves without having to be refocused, an operation which was apt to disturb its optical system and introduce errors. Alternate settings were made on the first and last lines of this restricted region and the mean of each was taken unless the readings showed that the set of waves was undergoing a general movement, as happens with a liquid whose surface tension is changing with time. In this case the difference between any particular reading and the mean of the preceding and succeeding readings gave the mean length of a known number of waves.

§ 5. THE RIPPLE METHOD AS A DYNAMIC METHOD

It was thought interesting to attempt to discover in what sense the ripple method of measuring surface tension could be called a "dynamic" method. Methods which have been described as dynamic include those of oscillating jets[21] and oscillating drops[22]. In all these the motion of the liquid surface is essential. The drop-weight, maximum bubble-pressure, and ring experiments ought to be included in the dynamic class since at the actual instant of rupture the surface is in motion, the rate of which is beyond the control of the experimenter. In the case of the method of oscillating jets, Rayleigh[23] made experiments which brought out quite clearly the dynamic nature of the method. He measured the surface tension of sodium-oleate solutions and found that the value obtained was that of pure water. Now sodium-oleate is positively adsorbed on to a water-air interface and its surface tension is that corresponding to a monomolecular layer of solute molecules provided that initially they are present in sufficient numbers in the bulk of the solution. The process of adsorption requires for completion a finite time which increases with dilution. This was measured by Bigelow and Washburn[24]. Rayleigh's results show that in the case of the oscillating-jet experiment the surface is renewed sufficiently rapidly to prevent an appreciable superficial concentration of sodium-oleate molecules from ever being established. Thus such a solution has two definite surface tensions, the truly dynamic and the truly static (such as might be determined by the method of capillary rise) and the results given by any particular method will give an indication of the degree of disturbance of the surface which the method entails. The only information of this kind which could be discovered in relation to the ripple method was that contained in a footnote on page 51 of the English translation of Freundlich's *Colloid and Capillary Chemistry*. This reads: "One might suppose that the method of surface waves leads to dynamic values. This is not the case as soon as the waves have formed properly. These new molecules of the liquid do not come continually into the waves; those remain, for the most part, which were originally present".

Consider what happens when the ripple method is used on a positively adsorbed solution. During the passage of progressive ripples over a plane surface the mean area of the surface will remain constant. There will, however, be a change in the area per small horizontal length dx, figure 3, taken along the direction of propagation. If dx is made small enough, the variation of surface area per dx is from $dx/\cos\phi$ to dx for an area of unit length perpendicular to the drawing, where ϕ is the maximum slope of the wave-outline.

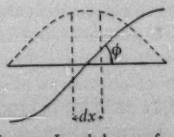

Figure 3. Local change of area due to passage of ripple.

If the wave is represented by

$$y = a \sin \frac{2\pi}{\lambda} (x - vt)$$

the maximum value of dy/dx (which is $\tan\phi$) is $2\pi a/\lambda$. Both a and λ can be arrived at from measurements, and $\tan\phi$ and consequently $\cos\phi$ can be evaluated. Thus

the fractional change of area which takes place in one-quarter of the period of oscillation can be calculated.

It must be emphasized, however, that although this change of area per very small horizontal length of surface takes place at all points on the surface, yet the area per half wave-length remains constant, and therefore even if at individual points the surface concentration of dissolved molecules is changed on account of momentary contraction or expansion the average concentration over half a wave-length remains constant and will depend upon time in exactly the same way as if the surface were stationary.

During the series of readings which is recorded later the amplitude of the waves did not exceed 0·00002 cm.* and the wave-length was approximately 0·2 cm. From this we find that tan $\phi = 0{\cdot}0006$ and cos $\phi = 0{\cdot}9999998$, so that the maximum local variation of area would be two parts in 10,000,000 and no greater change of surface tension than this would be expected even if the mobility of the dissolved molecules were so small that the change of area resulted in a proportionate change of concentration.

There is still the possibility that some disturbance of the surface structure other than that due to local change of area might result from the passage of waves over a surface. If such an effect is present, then the value of the surface tension given by the ripple method would be that for pure water, or it might lie between this value and the final equilibrium value given by a static method. In the latter case it would be expected to depend on frequency, i.e. upon the rate of disturbance of the surface. These points were investigated.

§ 6. MEASUREMENT OF SURFACE TENSION OF SOLUTIONS OF CETYL PYRIDINIUM BROMIDE

(i) *Aqueous solutions.* At about the time when the present work on the ripple method was in progress, Dr N. K. Adam† was measuring the fall with time of the surface tension of very dilute aqueous solutions of cetyl pyridinium bromide. He used a static method, namely that involving the measurement of the dimensions of a sessile bubble, in view of the fact that this method gives values of surface tension independent of contact angle. He found that after the formation of a bubble the surface tension fell at a decreasing rate, reaching a final value only after a week or so in the case of the most dilute solutions. Thus there was to hand a liquid whose rate of attainment of surface equilibrium was exceedingly slow, and Dr Adam kindly provided as much solution as was required.

When the necessary adjustments had been made and satisfactory images were visible in the telescope, the surface was swept four times with the barriers, a stop clock being started during the last stroke. The telescope was rapidly moved and focused until lines corresponding to waves of comparatively small amplitude were

* The method of estimating this quantity is described in the next paper.

† Both Dr Adam's results and those presented in this paper were brought to the notice of the Faraday Society during a discussion on colloidal electrolytes; see *Trans. Faraday Society*, **31**, 204 (1935).

visible in the field. The method of observation previously described was then used, the cross wires being set alternately on two lines one wave-length apart. This procedure was continued, readings being taken every half-minute, and the frequency of the oscillator was adjusted to the exact value as often as was necessary. The first setting could be made 1½ minutes after the fresh surface was formed. For the purpose of plotting a graph the average wave-length during successive intervals of not more than 8 minutes (and considerably less in the case of initial readings where the time change was more rapid) was calculated and recorded as the wave-length corresponding to the time centre of the interval. A graph of wave-length against time was then drawn. From this the smoothed values of the wave-length at certain convenient times were read off, the corresponding surface tensions were calculated and the final graph was thus constructed.

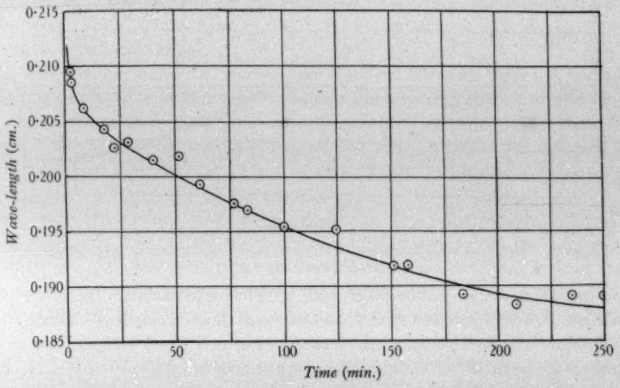

Figure 4. Change of wave-length with time. Aqueous solution of cetyl pyridinium bromide (0·003 per cent).

The curve, figure 4, shows the fall of wave-length with time for a 0·003 per cent solution at 20° C., the frequency of the ripples being 200 per second. Figure 5 is the corresponding {surface tension, time} curve. The observations shown extended over 4 hours. After 20½ hours the same solution was found to have a surface tension of about 36 dyne/cm. Two other solutions gave values 36 and 39 at 19 and 24 hours respectively. Other curves were taken, particularly during the initial hour, but figure 4 is the most uniform. In some cases it happened that at a particular time the wave-length curve showed discontinuities, the points in every case showing a jump upwards though the subsequent rate of fall was unchanged. This may quite well have been due to an outside disturbance which would tend to break up any surface structure that was responsible for the lowering of surface tension.

(ii) *Solutions of cetyl pyridinium bromide in N/20 sodium bromide.* It was shown by Dr Adam that if the cetyl pyridinium bromide was dissolved in very dilute

electrolyte solution (e.g. sodium bromide) the rate of attainment of equilibrium was very much increased. In fact, after 3 or 4 seconds there was no further fall of surface tension. Accordingly, a solution of strength 0·003 per cent in $N/20$ sodium bromide was made up and used in the ripple apparatus.

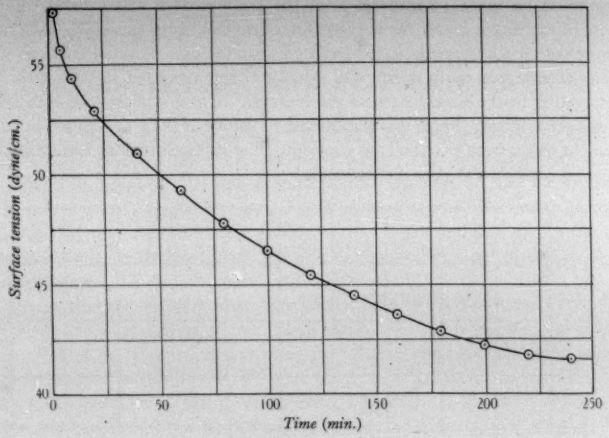

Figure 5. Change of surface tension with time. Aqueous solution of cetyl pyridinium bromide (0·003 per cent).

Since readings could not be taken until about 1½ minutes after the formation of the surface, no fall of surface tension was observed, the first readings yielding almost the minimum value. The solution was supersaturated at air temperature and all readings were made at 30° C. The results are shown in table 1.

Table 1. Surface tensions of solutions of cetyl pyridinium bromide in $N/20$ sodium bromide

Frequency		Age of surface (min.)	Surface tension at 30° C. (dyne/cm.)
Same solution	50	5	31·6
		23	31·6
	100	5	30·9
		36	29·4
		57	30·4
		160	29·9
	200	7	30·3
		21	29·1
	300	7	29·6
		26	28·3
		40	28·4
Different solutions	200	—	30·6
	300	6	31·4
		33	30·4

§ 7. DISCUSSION OF RESULTS

(i) *Aqueous solutions.* The surface showed a steady approach to equilibrium, the final value of surface tension being in agreement with that found by Dr Adam, 36 dyne/cm. The rate of attainment of the final value seemed larger than that found in Dr Adam's static experiments, but no definite deduction should be made from this because he remarks that his curves were not particularly reproducible and because, further, if the rate of formation of the stable surface depends on the diffusion of molecules, it must be influenced by convection effects which are almost uncontrollable in the ripple apparatus. The results do, however, show conclusively that as far as the solution used is concerned, the passage of waves of capillary dimensions over the surface has no retarding effect upon the formation of the surface layer. The ripple method is not therefore comparable with the oscillating-jet method in this connexion.

(ii) *Solutions in electrolytes.* These results confirm the static nature of the ripple method, not only because the values which it gives for the surface tension of the solutions are the same as those given by static methods but also because there is no change of this value with the frequency of the waves. Results for different frequencies do show some diversity, but it is not sufficiently large or regular to suggest a serious effect of frequency on surface tension.

It must be remembered that apart from the small gravity term the value of the surface tension is determined by the cube of the wave-length, and since for a frequency of 300 the wave-length is 1·26 mm. the variations of surface tension shown in the table may well be due to experimental errors.

(iii) *Damping of waves due to surface layer.* It was noticed that the waves extended down the tank for a much shorter distance in the case of the cetyl pyridinium bromide solutions than in the case of pure water. Moreover, as the surface tension fell, damping increased. Thus it seems that the surface layer occasions considerably greater damping than does a pure water surface. The bulk viscosity of the solution presumably does not vary appreciably with time, whereas the surface structure does. This leads to the deduction that the damping of waves of capillary dimensions is a function of the surface structure.

§ 8. ACKNOWLEDGMENTS

This work has been carried out in the Physical Laboratory of University College, London. The author wishes to thank Prof. E. N. da C. Andrade, F.R.S., for having provided facilities and for displaying a helpful interest in the progress of the research, and Dr N. K. Adam, F.R.S., for the tank and solutions.

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A METHOD OF MEASURING THE AMPLITUDE AND DAMPING OF RIPPLES*

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ABSTRACT. The optical arrangements of the author's ripple apparatus are such that determinations may be made of the amplitudes as well as of the wave-lengths of the ripples provided certain assumptions are made with regard to the wave-form. The fall of amplitude with distance of a maintained train of straight or circular waves is discussed, and the measurements taken show that the damping due to viscous forces causes a logarithmic falling off of amplitude. The damping factor is evaluated. In the case of circular waves the decrease of amplitude due to the spreading of the waves has to be taken into account. The amplitude of ripples which are satisfactorily observable is of the order of 2 or 3×10^{-5} cm.

§ 1. INTRODUCTION

In the literature relating to the ripple method of measuring surface tension very slight reference is made to the amplitude of the ripples employed apart from the statement of the condition that Lord Kelvin's equation[1] holds only for small amplitudes. Both Dorsey[2] and Watson[3] mentioned the fact that when successive troughs or crests are used as cylindrical mirrors during the usual performance of the experiment, their focal lengths increased with their distance from the source owing to decreasing amplitude; but neither author passed from this to a computation of the amplitudes involved, although Watson actually published enough data to enable a rough calculation to be made. He hazarded an estimate of the amplitude of the waves at the source, basing it upon a measurement of the amplitude of the source itself.

Gorter and Seeder[4] made the first measurements of amplitude by causing a parallel beam of light to fall normally on the ripple surface and observing the maximum angle between reflected rays. This gave the maximum angle between tangents to the wave outline, and hence the amplitude of the waves. Measurements were taken when thin films were present on the surface, and a decrease of amplitude was observed when the films were compressed.

It is the purpose of the present paper to show how the amplitudes of the waves at any distance from their source may be calculated from measurements which it is possible to make during the use of a ripple apparatus such as that employed by Dorsey, Watson or the present writer[5].

* The substance of this paper formed part of a thesis submitted for the degree of Ph.D. to the University of London.

§ 2. THEORY OF EXPERIMENT

The apparatus previously described[5] causes a parallel beam of light to fall vertically upon the liquid surface carrying the ripples. Focal lines are formed at the foci of the cylindrical mirrors comprising the troughs and crests. In the case of the troughs the images are real and are situated above the surface while those due to the crests are virtual and below it. In both cases the images move farther from the surface as the waves travel away from the source and their amplitude decreases.

Following Lord Kelvin, let us assume that the straight ripple may be represented by

y, a, λ, x, v, t

$$y = a \sin \frac{2\pi}{\lambda}(x - vt) \qquad \ldots\ldots(1),$$

and further that the regions of maximum curvature are responsible for the production of the images. Here no account is taken of damping, since in the following analysis it is only necessary that the amplitude (a) should be constant over a distance of half a wave-length.

We obtain from equation (1) the relationship that at any instant

$$\frac{d^2y}{dx^2} = -\frac{4\pi^2 y}{\lambda^2} \qquad \ldots\ldots(2),$$

and, since the amplitude is always small compared with the wave-length, the radius R of curvature R at a trough or crest will be numerically equal to the reciprocal of the maximum value of d^2y/dx^2, thus

$$R = \frac{\lambda^2}{4\pi^2 a} \qquad \ldots\ldots(3).$$

f The focal length f of the mirror corresponding to this radius will be given by

$$f = \tfrac{1}{2}R \qquad \ldots\ldots(4),$$

so that if f and λ are measured the amplitude may be calculated from equations (3) and (4), thus

$$a = \frac{\lambda^2}{8\pi^2 f} \qquad \ldots\ldots(5)^*.$$

In what follows we are concerned more with rate of decay than with precise values of amplitude and it is, therefore, only necessary to remember that

$$a = \frac{B\lambda^2}{f} \qquad \ldots\ldots(6),$$

B where B is a number.

By a well-known result in hydrodynamics we know that in the case of gravity waves the kinetic and potential energies per wave-length are equal, their sum being g, ρ equal to $\frac{1}{8}g\lambda a^2\rho$ per unit horizontal length perpendicular to the direction of propagation. The effect of surface tension may be allowed for by supposing that g is

* When amplitudes are small it might be permissible to treat the half-wave outline between two consecutive points of zero displacement as an arc of a circle and not as a sine wave. This leads to the result $a = \lambda^2/64f$.

increased by the amount $4\pi^2T/\rho\lambda^2$, which gives the total energy E per wave-length of ripples thus — T, E

$$E=\frac{a^2\rho\lambda}{2}\left\{g+\frac{4\pi^2T}{\rho\lambda^2}\right\} \quad \text{.....(7),}$$

or simply

$$E=\pi a^2\rho v^2 \quad \text{.....(8).}$$

Hence for a given liquid and a fixed frequency we can write

$$E=Ca^2 \quad \text{.....(9),}$$

where C is a constant. — C

In the case of straight ripples originating from an infinitely long dipper the action of viscous forces is the only factor influencing damping, which if assumed to be exponential may be represented by

$$E=E_0e^{-Kx} \quad \text{.....(10),}$$

where K is a damping factor applying to decay of energy with distance x from the dipper, and E_0 is the energy at the dipper. Remembering equation (9) and putting $k=\frac{1}{2}K$ we may connect the amplitude at any point x with that at (but not of) the dipper by the equation — K, x, E_0, k

$$a=a_0e^{-kx} \quad \text{.....(11).}$$ — a_0

Combining equations (11) and (5) we have

$$\frac{1}{f}=\frac{1}{f_0}.e^{-kx} \quad \text{.....(12),}$$

where f_0 is the focal length of the mirror whose amplitude is a_0. When natural logarithms are taken, equation (12) gives — f_0

$$\log f=kx+\log f_0 \quad \text{.....(13).}$$

Thus if the foregoing analysis is correct we should expect a graph of $\log f$ against x to be a straight line and the slope of the line will give us k.

With circular ripples we should expect a falling off of amplitude on account of the spreading of the waves, apart from the effect of viscous forces. The total energy associated with one complete wave of radius x will be $2\pi xE$ since E represents the energy per unit length. If the fluid had no viscosity this expression would be constant for all values of x. The effect of viscosity may be allowed for by writing

$$2\pi xE=De^{-Kx} \quad \text{.....(14),}$$

where D is a constant representing the total energy at $x=0$. — D

Combining equation (14) with equations (9) and (5) and taking logarithms we obtain

$$\log\left(\frac{\sqrt{x}}{f}\right)=-kx+F \quad \text{.....(15),}$$

where F is a constant. — F

Thus we should expect a graph of $\log\left(\frac{\sqrt{x}}{f}\right)$ to be a straight line and the slope should give us the value of k. For the same liquid and frequency the value should be equal to that given by equation (13).

In the observations which follow, logarithms have been taken to the base 10 and consequently the values of the slopes must be multiplied by 2·303 for the purpose of evaluating k.

§ 3. METHOD OF EXPERIMENT

The writer's ripple apparatus which is fully described in the previous paper was modified only to the extent of replacing the cathetometer telescope by one of another type which could be focused by rotating a knob. To this was attached a circular scale of arbitrary divisions, and a fixed pointer was placed above it. A small piece of squared paper was clamped at various known distances above the surface of the liquid in the tank and the image of the paper was focused in the telescope. Observations were taken which enabled a curve to be drawn connecting readings of the focusing-knob with the distance above the liquid surface of the point upon which the telescope was focused.

Straight ripples having been established, the experiment consisted in bringing into focus the lines seen in the telescope at various points along the length of the tank. It was not necessary to know the actual position of the origin of the ripples in order to obtain a value of k, but no measurements were taken at points nearer to the origin than 3 cm., because the surface became curved by capillarity within this region. The middle portions of the lines in the centre of the field were focused. Usually the telescope was moved until the cross-wire was situated centrally between two adjacent lines. The cathetometer vernier gave the reading against which the logarithm of the focal length of the ripples was plotted.

It being established that apart from the experimental error the graph of $\log f$ against x was a straight line, it was decided to take measurements designed for the direct calculation of k. Two points were chosen at a convenient distance apart, and settings of the telescope were made first at one point and then at the other. Any change of amplitude common to the whole surface, such as might be due to contamination or a change in the amplitude of the valve oscillator, would result in a change in the readings at both points. If such changes were not large the mean reading of the focusing-scale at each point was taken and k was deduced by dividing the difference between the logarithms of f at the two points by the distance between them.

Actually the amplitude of the oscillator was checked by allowing part of the band of light produced by the vibrating mirror to fall on a ground-glass screen and observing the positions of the extremities. Very little variation of amplitude was found. Another pair of points was selected and k was calculated for a second range of distance. A few experiments were made with circular ripples produced by a glass style attached to the end of the dipper reed. In this case since $\log(\sqrt{x}/f)$ enters into the calculations, x must be measured from the origin of the ripples. The experiment was conducted in the same way as for straight waves.

§ 4. PRELIMINARY RESULTS

Straight waves. Figure 1 shows results for water at 20° C., the frequency of the ripples being 300 c./sec. In taking the readings four or five settings of the focusing-knob of the telescope were made and the mean setting for each distance was taken. Before the telescope was moved to the next position the surface was swept. As is

indicated in the figure, settings were made first as the telescope was being moved away from the dipper and then as it was being brought back. The line drawn gives more weight to the points taken during the first half of the experiment than to the remaining points. The slope is 0·191 per cm.

Results of measurements made between two fixed points in the wave train are shown in table 1. The first two rows represent readings taken in succession. The third and fourth were recorded on different occasions.

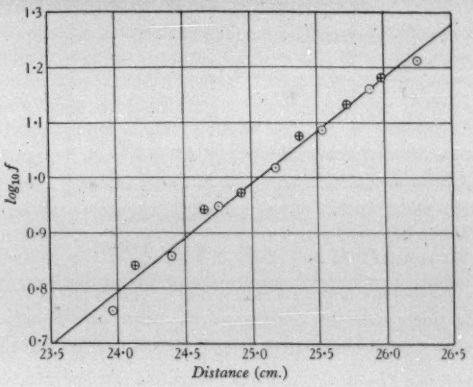

Figure 1. Damping of straight ripples; ⊙ distance increasing, ⊕ distance decreasing.

Table 1. Damping of ripples on distilled water at 20° C. Frequency of ripples, 300 c./sec.; wave-length, 0·172 cm.

Position of telescope (cm.)		Mean readings of focusing-knob		Focal lengths of ripples (cm.)		Slope, $\frac{\log_{10} f_p - \log_{10} f_q}{P-Q}$
P	Q	p	q	f_p	f_q	
25·75	23·78	1553	1062	14·50	6·02	0·194
25·23	24·28	1397	1154	11·98	7·78	0·197
25·74	23·70	1577	1060	14·90	6·02	0·194
23·39	21·68	1579	1103	14·91	6·83	0·198
					Mean	0·196

Each of the focusing-knob readings is the mean of at least ten observations. The focal lengths were, of course, read off from the calibration curve. From the mean value of the slope we find that $k = 0{\cdot}451$ per cm. For any particular value of the focal length of the ripples the amplitude is obtained immediately from equation (5); for instance, taking $f = 14{\cdot}50$ cm. from table 1 we obtain $a = 2{\cdot}6 \times 10^{-5}$ cm.

It is a matter of some surprise that ripples which can easily be observed in the usual experiments designed for that purpose should turn out to have such small amplitudes.

Circular waves. A few attempts were made to test equation (15), which should give a straight-line plot. Figure 2 represents a set of results. Again the temperature of the water was 20° C. and the frequency was 300 c./sec. The points seem

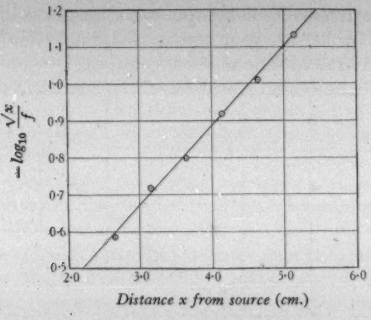

Figure 2. Damping of circular ripples.

to lie on a straight line the slope of which is 0·212. This is not in very good agreement with the slope given by straight waves. More careful experiments with circular waves are required before any definite statement can be made.*

§ 5. ACKNOWLEDGMENT

The author desires to thank Prof. E. N. da C. Andrade, F.R.S., for having granted facilities for the carrying out of this work, and also for the interest in it which he has displayed during its progress.

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* It is quite possible that, owing to the greater rate of decay of amplitude in the case of circular ripples, the assumption that amplitude is constant over a distance of half a wave-length is no longer permissible.

DISCUSSION OF THE PRECEDING TWO PAPERS

Dr G. F. C. Searle. An interference method of measuring the wave-length of the ripples may be possible. If a horizontal glass plate were placed close to the surface of the liquid, the interference bands seen with suitably interrupted green mercury light would be arranged in groups. The distance between the centres of successive groups could be measured.

Author's reply. Dr Searle's suggestion is ingenious but the experiment might, I think, be difficult, and the accuracy of the wave-length measurements would not exceed that obtained by the direct method. The amplitude of ripples used in surface-tension measurements is of the same order of magnitude as the wave-length of light, so that the fringes would be broad and few in number. The experiment might, however, be used as a means of checking measurements of amplitude.

Dr E. Tyler. The smallness of the fraction of the cycle during which the illumination persists suggests that the method is unsuitable for demonstration by projection on a screen. For projection purposes I have successfully employed a dual-reed synchronous arrangement in which one reed renders the light emitted by a 36-watt autolamp intermittent at mains frequency (50 cycles/sec.) before it falls on the ripple tank. This is made possible by bending the end of the maintained reed so that its end, when at rest, is coincident with the horizontal image of the lamp filament. The second reed, in series with the interrupter, is also operated from the same a.-c. supply, and carries the dippers; thus synchronization between the ripple formation and the intermittent illumination is automatically established.

It might therefore be an advantage to the author if he replaced the Pointolite lamp P', the slit S_1, and mirror M_1, by an autolamp reed interrupting device in the manner mentioned above. A slot may be fixed to the end of this reed if shorter times of flashing are required, but the question of width of slot is one of compromise with the amount of light available. The time of exposure required for photography is reduced considerably and there is no need to use ultra-fast plates. With Imperial Process Eclipse Plates, speed 650, successful photographs can be obtained with exposures ranging from 1 to 4 seconds. As regards measurement of the photographs, has the author tried photographing a graduated glass scale placed in the plane of the ripple surface, the image obtained being used for calibration purposes in evaluating λ?

A photocell traversing device might also prove useful in this connexion. The adoption of modern electric discharge tubes as stroboscopic illuminants may be recommended in certain cases for ripple-tank work. Both the Edgerton stroboscope* and B.T.H. stroboscopic discharge tube† serve admirably in this respect. I hope to demonstrate shortly some of the effects obtained with various types of discharge-lamp sources. Finally the author refers to the more thorough exploration into the

* Pamphlet, General Radio Co., Catalogue G, part 2, pp. 178–179 (March 1934), Cambridge, Mass.

† *Physical Society Exhibition Catalogue*, p. 165 (Jan. 1936).

possibilities of the vibrating reed idea for producing an intermittent beam of light. May I add that in this direction the use of the autolamp reed arrangement for producing a beam of intermittent light at a standardized frequency (50 c./sec.) has been successfully employed by me in the following ways, reference to which is made in a recent article.* (*a*) For the stroboscopic measurement of speed. (*b*) As a time base in a photographic falling-plate method for determining *g*. (*c*) As a stroboscopic illuminant in the study of falling liquid drops. (*d*) For visual demonstration of the nature of a transversal wave. If intermittent light is allowed to pass through a narrow aperture in a fixed screen and the resulting beam then falls on a piece of cardboard capable of being vibrated by hand, an apparently stationary transversal luminous wave system will be observed by persistence of vision between the screen and the cardboard.

AUTHOR'S reply. Some years ago I set up the ripple experiment for measuring surface tension using a reed carrying a slit, the line source being a stationary illuminated slit. In this I was following closely the technique described separately by Dorsey, Watson and Barnett. Dr Tyler uses a straight filament instead of an illuminated slit. In suggesting that the method described in the present paper was a novel one, I was referring to the use of the vibrating mirror rather than to that of the reed, which is, of course, a cheap and simple substitute for a tuning fork.

Whatever system of observation is used the fraction of the wave-length through which the ripple moves while it is being observed is that fraction of the time period for which illumination takes place. In my apparatus this may be reduced almost indefinitely. To achieve the same result with a vibrating slit requires such narrowness of the slit that optical adjustment may become difficult.

It should be remembered that in surface-tension work ripples of small amplitude are required, whilst those used in demonstrating the properties of wave-motion usually have much larger amplitudes. This is shown by the fact that the camera or other optical apparatus used in demonstrations requires to be focused on the liquid surface, whereas with ripples suitable for surface-tension measurements the images observed are at distances up to 30 cm. from the surface. Figure 2 in the first paper shows lines of considerable breadth, although the time of illumination was suitably reduced. This is because the ripples were shallow. With larger amplitudes cross-wire sharpness is easily obtained.

Dr Tyler's question regarding the measurement of wave-lengths by photography raises an interesting point which I once investigated. I tried for some time to measure wave-lengths with the help of a telescope having a fixed central cross wire and, parallel to it, another one which could be moved by means of a graduated screw which was calibrated by placing a scale in the plane of the images observed, and not in the surface as Dr Tyler suggests. The results were considerably in error because whereas the central image in the plane of the cross wires was formed by reflection from a crest, the adjacent one was formed by reflection from a point

* Tyler, *School Sci. Rev.*, pp. 238–239 (Dec. 1935).

slightly displaced from the crest of the next wave. This must be so since both reflected rays cross at the optical centre of the telescope objective. A correction was attempted and was partially successful, but this method of observation was finally abandoned. This kind of error is, it seems to me, necessarily present in any experiment involving the photography of ripples with a camera.

The new stroboscopic discharge lamps are remarkable and will probably be very useful in demonstrations of ripples, particularly if they can be operated independently of the a.-c. supply so that by slightly changing their frequency, while that of the ripples remains constant, the student may be enabled to distinguish between progressive waves and standing patterns. I shall look forward with interest to Dr Tyler's demonstrations.

539.165

THE β-RAY SPECTRA OF SOME INDUCED RADIOACTIVE ELEMENTS RESULTING FROM NEUTRON BOMBARDMENT

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ABSTRACT. A preliminary determination of the energies of the end points of the β-ray spectra of some unstable elements produced artificially by neutron bombardment was made, a cloud chamber being used. Although these energies are for the most part considerably higher than those encountered in natural β activity, they fit the Sargent curves fairly well.

Between 4 and 10 per cent of the tracks observed are positively curved. No evidence is available to explain their origin unambiguously.

§1. INTRODUCTION: THE SCOPE OF THE EXPERIMENTS

The periods of the β-ray disintegration of many new elements resulting from neutron bombardment have been determined recently by Fermi and his collaborators[1], and by others. The discovery of these new unstable nuclei has greatly extended the scope for investigations relevant to the new theories of β-ray decay; so we have used the method of the cloud chamber to find the sign of the charge of the particles in some cases where this was not previously known and to make a preliminary determination of the upper limits of the β-ray spectra of some of the more active of these elements.

In principle, this method gives immediately the complete disintegration curve for an element. However, with the radon sources available—about 100 millicuries—we could get a convenient number of tracks on each photograph by taking as much as possible of each element for activation. Consequently the sources used were *thick*, and so the shapes of our curves below the maxima are completely wrong, and the maxima themselves are probably slightly displaced.

§2. EXPERIMENTAL DETAILS

The automatic cloud chamber used is similar in design to one recently described by C. T. R. Wilson[2]. A rubber diaphragm, acting as a piston, moves below a fine wire gauze which constitutes the floor of the chamber. The expansion was obtained by suddenly evacuating the space below the diaphragm, the required volume-ratio being secured by limiting the final position of the diaphragm by means of an adjustable disc. In this way we could use the automatic mechanism devised by Blackett[3] for Wilson's earlier form of cloud chamber.

A magnetic field of 1000 gauss, uniform to 1 per cent over the illuminated part of the chamber, was provided by water-cooled solenoids. The tracks were about 5 cm. long. The method of illumination used—that of a flash from a mercury lamp activated by a current from a transformer—has been described by Blackett[4]. A pair of photographs was taken at each flash by cameras inclined at 90 and 75° to the plane of the chamber.

A cylindrical pot, of diameter 1·5 cm., made of very thin metal foil was let in axially through the top of the chamber. It was made long enough to reach the gauze so that the distortion of tracks due to the swirls that it is liable to produce in the gas would be minimized.

The elements were always prepared, either as foils or as powders wrapped in cellophane, in cylindrical form to fit nicely inside the pot. They were activated by the neutrons from radon-beryllium sources about 100 millicuries strong, those showing the "water effect" being activated in a cavity in a large paraffin wax block. After sufficient time they were transferred to the pot, and expansions were made while the activity persisted.

§3. RESULTS

Of the tracks obtained, those showing small angular deviations, together with all short tracks, were carefully rejected according to a definite criterion such as was used by Champion[5]. Then the strongly curved tracks were measured by fitting to them circular arcs of known radii photographed on slides, while for those less curved, the traversing-microscope method described by Anderson[6] was adopted.

The results of these measurements are shown in the form of block diagrams in figure 1. From the smooth curves drawn through these the end points have been very roughly determined, and are collected in table 1. However, the determination of the end points in this way is largely arbitrary.

Table 1

Element	Isotopes	Half-period studied	Upper limit of β-ray spectrum
9 F	19	9 S.	$7 \pm 2 \times 10^6$ eV.
14 Si	28, 29, 30	2·3 m.	$4 \pm 0{\cdot}5 \times 10^6$
45 Rh	103	44 S.	$3{\cdot}6 \pm 0{\cdot}5 \times 10^6$
47 Ag	107, 109	23 S.	$3{\cdot}8 \pm 0{\cdot}5 \times 10^6$
		2·3 m.	$2{\cdot}8 \pm 0{\cdot}4 \times 10^6$
63 Eu	151, 153	9·2 h.	$2{\cdot}6 \pm 0{\cdot}4 \times 10^6$
66 Dy	161, 162 163, 164	2·5 h.	$1{\cdot}9 \pm 0{\cdot}2 \times 10^6$

The effect of errors in the curvature-measurement is to increase, in general, the number of tracks in the higher-energy groups, and to produce extra blocks beyond the true end points. By far the most serious of these errors is that arising from the distortion of tracks due to swirls in the gas of the chamber; these may completely falsify the estimation of high energies. The curvature of a 10-million-volt track—e.g. one in the middle of the tail extending beyond the end point of the

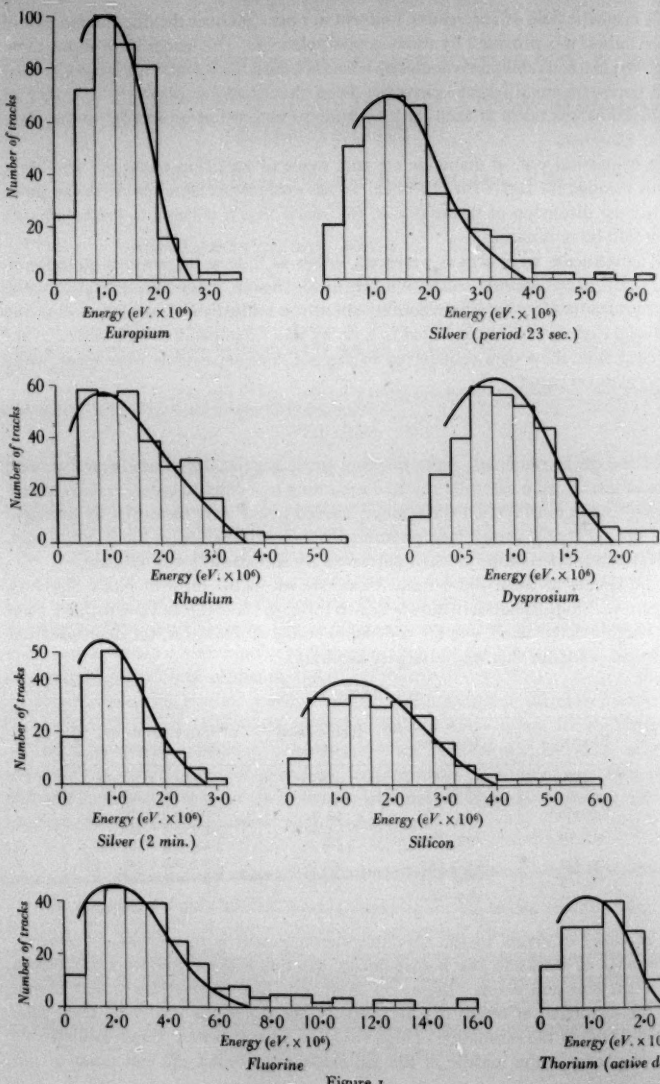
Number of tracks
Energy (eV. × 10⁶)
Europium
Silver (period 23 sec.)
Rhodium
Dysprosium
Silver (2 min.)
Silicon
Fluorine
Thorium (active deposit)

Figure 1.

spectrum of activated fluorine—is about 0·6 in arbitrary units. An analysis of β-ray tracks taken without a magnetic field showed that, as a result of this swirl distortion, our curvature-measurements were liable to an error of 0·2 units, or over 30 per cent for this case. We estimate the total probable error from all causes as being nearer 40 per cent. For the spectra of activated silicon and silver it is about 15 per cent. The long tails on the high-energy side of the spectra of these elements may then be entirely spurious, being due to this effect. Although some of the tracks may truly correspond to high-energy particles produced by the γ rays of unknown energy known to accompany the disintegrations, the end points obtained from the smooth curves will still have this uncertainty. These views are confirmed by an analysis of some photographs of the β rays from a source of thorium active

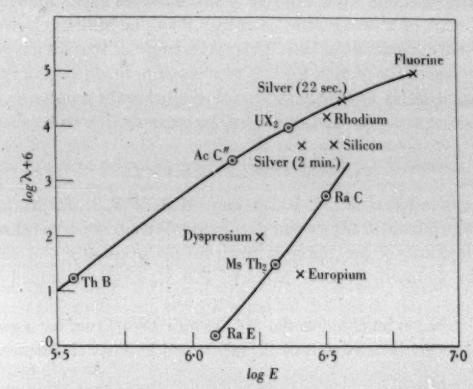

Figure 2.

deposit. The continuous spectrum has an end point of 2·2 million volts, and there is also a strong γ ray producing photo-electrons up to 2·63 million volts. We found a tail extending to 2·8 million volts, and an upper limit at 2·3 million volts; the probable error was expected to be about 10 per cent. The probable errors given in table 1 are determined from these considerations. That associated with the spectrum of activated fluorine is so large as to make the determination for this element practically worthless; further experiments with improved technique will be undertaken.

In figure 2 the logarithms of the end points are plotted against the logarithms of the corresponding decay constants to form Sargent curves[7]. The points seem to fall as well as might be expected about one or other of the two curves, especially as the end points given above are probably too high. The accuracy of the determination of the spectra is insufficient to justify any more elaborate comparison with theory.

§4. POSITRON TRACKS

For every element studied we have always found a few per cent of the tracks apparently coming from the source, but with positive curvature. By a rough estimation of the retrograde electron tracks from the walls of the cloud chamber one might account for a fraction of the positively curved tracks observed. But in some cases, e.g. europium, these apparent positrons constitute as much as 10 per cent of the measured tracks, and it is difficult to give an unambiguous answer to the question of the origin of these tracks. Further experiments are in progress to elucidate this question.

No certain case of the production by an electron of a positron-electron pair in the gas has been observed. In the course of this work we have photographed about 100 metres of track of β rays greater in energy than one million electron-volts and have observed only one doubtful case. This result suggests that for oxygen the upper limit of the average cross-section for this process of positron production by β rays, if it takes place at all, is less than 10^{-23} cm^2. Skobelzyn[8] reports several cases of such production of positrons and estimates the cross-section to be about 10^{-23} cm^2.

§5. ACKNOWLEDGMENTS

We wish to thank Prof. P. M. S. Blackett, M.A., F.R.S., for his help in many ways, and for much fruitful advice and discussion. We also wish to acknowledge the courtesy of Mr Alton of the Radium Institute for preparing and supplying the radon-beryllium sources. Prof. S. Sugden, F.R.S., kindly supplied us with the rare earths.

One of us (R. N.) is indebted to the Sir Dorabji Tata Trust for a grant, and the other (R. E. S.) to the Department of Scientific and Industrial Research.

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REVIEWS OF BOOKS

A Source Book in Physics, by WILLIAM FRANCIS MAGIE. Pp. xiv + 620. (McGraw-Hill Publishing Co., Ltd.) 30*s*. net.

The volume under review is a valuable contribution to the history of physics. It attempts to bring before the reader a picture of the outstanding events in the progress of science by supplying quotations selected from the publications of the pioneers when they announced their discoveries to the world. It will prove of great assistance to the mature student and the teacher as a reference work. Furthermore it can be dipped into with the assurance that it is never dull.

Opening the book at random one finds for example a quotation from Cailletet who, whilst directing his father's foundry at Châtillon-sur-Seine, carried out the relatively simple experiments which proved that oxygen could be liquefied. These experiments preceded by only a few weeks the more elaborate ones at Geneva of Pictet, whose discovery was communicated to the French Academy in the despatch "Oxygen liquefied to-day under 320 atmospheres and 140° of cold by sulphurous acid and carbon dioxide in succession".

Fizeau at the age of 30 describes the first successful attempt to measure the velocity of light by means of observations that do not involve astronomical constants. He says "These first trials furnished a value of the velocity of light only a little different from that which is accepted by astronomers. The mean value determined from twenty-eight observations which have been made up to this time is 70948 leagues of 25 to the degree".

To anyone wishing to become acquainted with the style of writing of Galileo, Newton, Lagrange, Cavendish, Ampère, Davy, Joule, Kelvin, Maxwell, Fizeau, Faraday, Curie, Crookes, or Roentgen, to mention but a few, the volume affords the means with the least amount of trouble.

The author of the work is to be congratulated on having made a very useful contribution to the literature of physics.

E. G.

Praktische Physik, by F. KOHLRAUSCH. Pp. x + 958. (Teubner, Leipzig.) RM. 24, in England.

Kohlrausch's *Praktische Physik* is an old friend whose first acquaintance some of us made in our student days. Successive editions of this useful handbook have faithfully mirrored the changes which are taking place with time in the domain of practical physics. Many an expert has contributed his quota to build the present imposing structure based on the foundations so truly laid by Kohlrausch single-handed in 1872. The general editor of the volume under review is Dr Henning and several of his collaborators are members of the staff of the Physikalische-Technische Reichsanstalt.

Written by men whose daily work is to make measurements under conditions where accuracy and convenience counts for more than mere novelty of method, this volume is characterised by discrimination and judgment that have been exercised in the selection and presentation of the material. It is a most valuable work of reference and the contributors are to be congratulated on the production of such a comprehensive treatise.

E. G.

Organic Solvents: Physical Constants and Methods of Purification, by ARNOLD WEISSBERGER and ERICH PROSKAUER. Translated from the German manuscript by RANDAL G. A. NEW. Pp. 212, including subject index and bibliography with 60 references to books and 1406 to periodicals. (Oxford University Press.) 15*s*.

A self-evident fact that has not always been acted on in the past is that the reliability of a number purporting to represent a physical constant of an organic liquid depends not only on the accuracy with which the measurement is made but also on the purity of the liquid. The determination to many decimal places of a physical constant of a *pure* organic solvent is a great achievement and of permanent value, but such a number is a double-faced villain if water or one or more of a host of possible organic impurities contaminate the liquid on which the experiment is made. The authors of this book rightly point out that there is an "ever increasing demand for variety and purity in organic solvents", and wide-spread gratitude will be felt towards them, one an organic chemist and the other a physical chemist, for compiling this compact treatise, which possesses an admirable structure. The general appearance of the pages is attractive and the descriptive passages have been lucidly translated.

The purification and physical constants of one hundred and fifty-seven organic liquids are discussed. These liquids are classified as hydrocarbons (aliphatic saturated, aromatic, aliphatic unsaturated), compounds with one type of characteristic atom or group (hydroxy-compound, esters, amines, etc.), and compounds with more than one type of characteristic atom or group (esters of hydroxyacids, etc.) and an intensive search has been made for the best values available of the following physical constants: molecular weight, density, melting- or freezing-point, boiling-point, vapour pressure, latent heat of evaporation, specific heat, cryoscopic constant, ebullioscopic constant, viscosity, electrical conductivity, dielectric constant, dipole moment, refractive index, ultra-violet absorption, infra-red absorption, and flash point. Clearly there are very few physicists who will not find such a book as this useful at some time or other, and it should certainly be near at hand when organic liquids are being used in quantitative experiments.

T. M.

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 48, PART 3 *May* 1, 1936 NO. 266

66.094.1:668.731.4 662.743

SOME THERMAL AND ELECTRICAL ASPECTS OF THE DESIGN OF CONVERTERS FOR THE HYDROGENATION PROCESS

BY A. BLACKIE, M.A., F.INST.P., C. W. OCKELFORD

AND

C. M. CAWLEY, PH.D., M.SC., A.R.C.S., D.I.C.,

ERRATA

"Thermochemical properties of nitrous oxide", by T. CARLTON-SUTTON, H. R. AMBLER and G. WYN WILLIAMS, *Proc. phys. Soc.* **48**, 189 (1936).

P. 193. In the footnote to table 3, *after* "water equivalent" *insert* "of contents".

P. 196. In the last column of table 6, *for* "3438" *read* "3348".

Pp. 196–8. *For* "cal./mol." *read* "kcal./mol." *or* "Cal./mol." throughout (10 occasions).

In problems in the hydrogenation of tar and coal which have been encountered in experimental work at the Fuel Research Station.

When a coal is heated in a retort the complex molecules of the coal substance split up, yielding as main products of the carbonization (*a*) lighter hydrocarbon gases together with H_2, CO, CO_2 and H_2S, etc.; (*b*) water which condenses as "liquor", containing a small proportion of ammonia, phenols, etc.; (*c*) tar, a mixture of heavier hydrocarbons, phenols, bases, etc.; (*d*) coke, which contains the greater part of the carbon present in the coal.

The quantity and composition of these products varies with the type of coal and the temperature at which the carbonization is carried out.

If, however, the coal is heated at about 450° C., a temperature lower than that normally used in carbonization, in the presence of hydrogen at high pressure (about 200 atmospheres), destructive decomposition is avoided to a very large

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ABSTRACT. A brief description is given of the hydrogenation process as applied to coal and tar, and some of the physical requirements in the design of apparatus and in the working of the process are enumerated. The final designs of converters with internal electric heating are described and a general account of the experiments carried out with a view to improving the thermal insulation, reduce the power consumption and decrease the temperature of the converter walls, is also given. The methods of maintaining a uniform temperature in the catalyst bed, and of dissipating the heat evolved by the reaction, which is strongly exothermic, are considered, and the experimental work is described. In the last section an account is given of the methods adopted to overcome the difficulties associated with electrical insulation.

§ 1. INTRODUCTION

IT may be of interest to members of the Society to have an account of the physical problems in the hydrogenation of tar and coal which have been encountered in experimental work at the Fuel Research Station.

When a coal is heated in a retort the complex molecules of the coal substance split up, yielding as main products of the carbonization (*a*) lighter hydrocarbon gases together with H_2, CO, CO_2 and H_2S, etc.; (*b*) water which condenses as "liquor", containing a small proportion of ammonia, phenols, etc.; (*c*) tar, a mixture of heavier hydrocarbons, phenols, bases, etc.; (*d*) coke, which contains the greater part of the carbon present in the coal.

The quantity and composition of these products varies with the type of coal and the temperature at which the carbonization is carried out.

If, however, the coal is heated at about 450° C., a temperature lower than that normally used in carbonization, in the presence of hydrogen at high pressure (about 200 atmospheres), destructive decomposition is avoided to a very large

extent. The primary products of decomposition, which at atmospheric pressure would decompose further or polymerize, are stabilized by hydrogenation. The result is that a large proportion of the coal substance is converted into oil.

When tar is treated with hydrogen, at 480° C. at a pressure of 200 atmospheres, a similar process occurs. The cracking which tar would ordinarily undergo at atmospheric pressure at this temperature is so modified by the presence of hydrogen under pressure, that the tar is converted into lower-boiling oils mainly hydrocarbon in nature. During the process the oxygen, nitrogen and sulphur in the raw material are converted into water, ammonia and hydrogen sulphide.

It has been found that the process of hydrogenation is much improved and accelerated by the presence of certain catalysts, of which tin is very effective for the treatment of coal, and molybdenum for the treatment of tar.

In the hydrogenation of coal, the catalyst in a powdered form is usually supplied to the converter as a constant proportion of the coal; only a very small amount of catalyst is required, and recovery is unnecessary. For the treatment of tar, however, a larger proportion of catalyst is needed. It has thus been found desirable to support the catalyst on a porous material through which tar and hydrogen are passed continuously. In this way, the necessity for recovering the catalyst is avoided. The catalyst-support which has so far been found most suitable is ignited alumina gel. This is impregnated with ammonium molybdate, which becomes converted during the hydrogenation process into molybdenum sulphide, the most active molybdenum catalyst[1].

A few typical results obtained by means of a single treatment of coal and low-temperature tar are given in table 1.

Table 1

Material	Coal	Low-temperature tar
Reaction temperature (°C.)	450	450–480
Reaction pressure (atmospheres)	200	200
Yields of products (per cent by weight of raw material)		
Spirit boiling up to 200° C.	20	45
Oil boiling above 200° C.	57	44
Gas	8	8
Water	10	8
Unconverted coal (ash, etc.)	10	—
Hydrogen absorbed (per cent by weight of raw material)	5	5

The oil distilling above 200° C. may be re-treated and converted into light spirit, when it gives a total yield of motor spirit amounting to 65 per cent by weight of coal and 80 per cent by weight of tar.

The hydrogenation process must be conducted in a converter able to withstand very high pressures, but, for reasons explained later, the pressure vessel or converter must not, in a commercial process, be subjected to the full reaction temperature. Experiments have therefore been carried out at the Fuel Research Station with the

object of designing a converter heated internally by electrical means and so thermally insulated that while the reaction chamber is maintained at a temperature of 480° C. the walls of the converter do not exceed a temperature of 100° C. In the present paper descriptions are given of converters that have been evolved for the treatment of low-temperature tar, or distillates from high-temperature tar, under the conditions of temperature and pressure already mentioned. The principles involved and the experimental results obtained may also be applied to the design of a converter for the treatment of coal.

The earlier work at the Fuel Research Station was carried out in converters heated externally by means of gas or electricity. The wall of the converter was in consequence raised to the temperature of reaction. With ordinary steels there is a considerable reduction of strength at this temperature and this necessitates a much more massive construction to ensure the requisite factor of safety. More important, however, is the fact that hydrogen, at the high pressure and temperature employed, rapidly causes decarburization of the steel, leading to the formation of cracks which start from the inside of the converter and soon so seriously diminish its strength that replacement becomes imperative. This form of attack is described in a paper by Barber and Taylor[2] which deals with the engineering side of this work at the Fuel Research Station.

The harmful results of hydrogen attack were reduced to a large extent by the use of certain alloy steels. Externally heated vessels are still therefore used for small-scale experimental work on the effect of various factors, such as temperature, pressure and time of contact, in view of the fine degree of temperature-control which it is possible to obtain in such converters.

The question of temperature-control raises several points of fundamental importance. The reactions occurring during the hydrogenation of tar are very susceptible to change in temperature, and, to a lesser degree, to change in pressure, and are markedly exothermic. The exact value of the exothermicity has not been determined because sufficiently accurate weight balances and calorific values of the raw materials and products are not at present available. It is hoped, however, to make some direct determinations of this heat of reaction in a specially designed converter-calorimeter. At present, from calculations based on the experimental observation that, when low-temperature tar is treated in an internally-heated converter, the heat of reaction is approximately equal to the heat required to raise the raw materials to reaction temperature, it is thought that the heat of reaction is of the order of 300 calories per gram of tar. Clearly the economic utilization of the heat of reaction, not accomplished in an externally-heated converter, is a vital consideration for a commercial process.

The requirements of a commercial process may now be summarized as follows. (1) The process should be continuous; (2) heat should be conserved as far as possible; (3) the temperature of the converter should be below that at which hydrogen attack becomes serious; and (4) the quantity and distribution of heat (and hence the reaction temperature) should be accurately controllable.

It was considered that these requirements would be satisfied by the use of an

electrically-heated cylindrical reaction chamber situated within a concentric pressure-resisting converter and thermally insulated therefrom. In the present paper the design of a suitable converter is described and some account of the difficulties encountered during its evolution is given also.

§ 2. DESIGN OF CONVERTER AND REACTION CHAMBER

Since the catalyst deteriorates gradually during use, it is necessary periodically to remove and reactivate it. It was thought desirable therefore that the arrangement of the converter should be such as to permit the removal of the catalyst without causing any disturbance to the heating units or the electrical connexions. In practically all the arrangements that were tried, it was accordingly adopted as an essential principle that the heating units should be wound on a cylindrical tube separate from the catalyst chamber. A satisfactory design incorporating this principle was evolved and is described below; a diagram of the arrangement is given in figure 1.

The converter, i.e. the outer, pressure-resisting vessel, is of mild steel 4 ft. long and 8 in. internal diameter. The walls are $1\frac{1}{4}$ in. thick and the flanges and end-covers respectively 1 ft. 4 in. in diameter and $3\frac{1}{4}$ in. thick. Mechanical details such

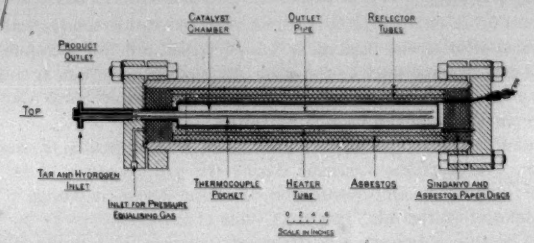

Figure 1.

as the method of making joints have been given elsewhere[2]. The catalyst or reaction chamber is also of mild steel and is 3 ft. 3 in. long and 3 in. in internal diameter; it is suspended from the top end-cover and hangs concentrically within the converter. Fixed eccentrically within the catalyst chamber are a thermocouple pocket and an outlet pipe for the reaction products, which pass down to the bottom. The pocket accommodates three thermocouples. Tar and hydrogen are fed into the top of the chamber through an annulus surrounding the thermocouple pocket and outlet pipe. Six radial metal conductors are placed within the catalyst bed and serve to assist in distributing the heat uniformly throughout the catalyst.

Surrounding the catalyst chamber, but not in contact with it, is the heater tube which is supported on, but electrically insulated from, the bottom cover. The tube is wound with three heating units, each of nine ohms resistance and consisting of no.16 s.w.g. Brightray wire, and respectively 10, 20 and 8 in. long, the smallest being at the bottom and the largest in the centre. The heating units are insulated

from the tube by layers of mica and asbestos paper and are covered with fireclay. The electric current in each heater is controlled separately by means of external resistances. The electrical connexions, six in all, are carried through the bottom end-cover and insulated therefrom by a method to be described later. The annular space between the heater and the wall of the converter is filled with thermal insulation material consisting of asbestos paper wound on three concentric, cylindrical, chromium-plated brass tubes; the innermost of the latter fits closely on the insulation material wound on the heater. The ends of the catalyst chamber are insulated from the cover of the converter by means of pads of sindanyo and asbestos.

With this arrangement the catalyst chamber is completely isolated from the insulation space so that the latter is kept free from hydrocarbon gases and moisture formed during the reaction; earlier designs allowed the reaction vapours free access to the insulation space. For the purpose of maintaining equality of pressure the insulation space is connected by an external line to the hydrogen supply or other gas at the same pressure. It is not necessary, therefore, to construct the catalyst chamber as a pressure-resisting vessel.

In addition to good electrical and thermal insulation, the advantages of this apparatus are that the electrical connexions are made at the bottom cover and all the pipe connexions at the top, so that by lifting the latter the catalyst chamber may be withdrawn without disturbing the electrical heater.

As a modification of this type of converter, a further apparatus which has some advantages was designed and tested. This second converter differed mainly from the first in that the electric heaters were wound directly on the outer surface of the catalyst chamber and covered with half an inch of thermal lagging. By this device heat was applied more directly to the chamber, so that the heating element could be run at a lower temperature with consequently less deterioration of the electrical insulation. As the lagging over the heater was also increased by this arrangement, the thermal losses were reduced.

The catalyst chamber had the same internal dimensions as that used in the apparatus first described; the thermocouple pocket and the pipes for the introduction of tar and hydrogen and for the removal of products were similarly unchanged.

The advantages of this modified arrangement are that the power-consumption is reduced and the life of the electric heater increased; the disadvantage is that the removal of the catalyst chamber involves the removal of and possible damage to the heater. The relative importance of the advantages and disadvantages depends upon the nature of the process for which the converter is employed and particularly upon the frequency of replacement of the catalyst.

The throughputs of tar and hydrogen in these plants were normally 1600 ml. and 1700 litres per hour respectively. In certain runs made with approximately the same internal and external temperatures the tar rates were varied from 1200 to 2000 ml. per hour with corresponding rates for the hydrogen, and it was found that the same power input was required. It follows that the heat of the exothermic reaction is sufficient to heat the raw materials to reaction temperature; the electric power supplies the heat loss from the converter.

§ 3. PROBLEMS RELATING TO THERMAL INSULATION AND THE CONTROL OF TEMPERATURE IN THE CATALYST CHAMBER

Thermal insulation. A number of experiments were made on the efficacy of various forms of thermal insulation in the annular space between the outer surface of the heater and the inner surface of the walls of the converter. Some of the earlier of these experiments were made with a converter similar to those already described but of small dimensions, namely length 3 ft. 6 in. and internal diameter 6 in. The walls were 1 in. thick, the flanges $2\frac{1}{2}$ in. thick and the end-covers $2\frac{3}{4}$ in. thick. The diameter of the catalyst chamber was 3 in. The results of some experiments made in this smaller converter are given in table 2.

Table 2

Experiment	Temperature (°C.) at				Power required (kW.)
	centre of catalyst chamber	top cover outside	middle of converter outside	bottom cover outside	
(*a*) Reflector tubes unpolished. Air at atmospheric pressure	440	64	104	60	1·01
(*b*) Reflector tubes chromium-plated and polished. Air at atmospheric pressure	456	57	74	53	0·75
(*c*) As in (*b*) but with hydrogen at atmospheric pressure	452	78	140	68	1·61
(*d*) As in (*c*) but with hydrogen at 200 atmospheres	440	192	220	122	4·57
(*e*) As in (*d*) but with aluminium foil and asbestos paper between inner and outer reflectors	474	188	220	128	4·30
(*f*) As in (*e*) but with aluminium foil and asbestos paper in space between outer reflector and converter wall in addition. Process run with hydrogen contaminated with hydrocarbon vapours	500	139	155	143	3·25
(*g*) As in (*f*) but with extra asbestos in outer annulus	490	126	150	141	2·81

In experiment (*a*) the annular space surrounding the catalyst chamber contained two concentric steel cylinders which served as reflecting tubes to reduce the loss of heat by radiation and convection. Experiments (*a*) and (*b*) show the reduction in power-consumption and surface temperature due to decrease in the transfer of heat by radiation brought about by the chromium-plating of the reflector tubes.

Experiments (*b*) and (*c*) show the effect of replacing the air by hydrogen at atmospheric pressure and the resulting increase in surface temperature and power-consumption due to the increased conduction and convection. Experiments (*c*) and (*d*) show the enormous effect of the greatly increased convection due to increasing the pressure of the hydrogen.

A consideration of these experiments led to the conclusion that the major part of the heat-loss was due to internal convection. It can be shown that to reduce convection to negligible proportions the size of the gas-filled interspaces in an insulator when these are filled with hydrogen at a pressure of 200 atmospheres must be very much smaller than when they are filled with air at atmospheric pressure. As the dimensions necessary are very much smaller than can be obtained in practice by increasing the number of reflector tubes, it was decided to fill the space between the two reflector tubes with alternate layers of aluminium foil and asbestos paper, free spaces in this zone being thus reduced to negligible dimensions. The aluminium foil is impervious and acts moreover as an additional reflector and yet is so thin that the increased conductivity is small. That the whole available space was not filled in this experiment was a compromise, as at this stage it was desired to preheat the hydrogen by making it traverse the insulation space before entering the catalyst chamber. The result of this packing is shown in experiment (*e*) which may be compared with experiment (*d*). At first sight the improvement appears slight, but in this experiment it must be noted that the temperature in the catalyst chamber was 474° C. as compared with 440° C. and the saving in power was in reality more than that shown.

At a later stage when the attempt to preheat the hydrogen by this method had been abandoned, the space between the outer reflector tube and the converter wall was also packed with asbestos and aluminium foil, and a process run, in which tar and hydrogen were treated, was carried out. In this apparatus the reaction products were discharged through a perforated plate at the end of the catalyst chamber into an open cup, from which they were conducted by a pipe through the bottom end-cover of the converter. The annular insulation space was thus accessible to the gaseous reaction products. The marked improvement shown by experiment (*f*) was therefore due in part to the fact that the insulation space contained a mixture of hydrogen with hydrocarbons of lower conductivity. The importance of restricting convection is again shown, however, in experiment (*g*) in which an improved packing of the thermal insulation material resulted in a further reduction of power.

At a later stage further process experiments were carried out in the larger converter of the type already described on p. 342. The internal arrangement of this was again such as to allow the products free access to the insulation space. The results of the experiments are recorded in table 3.

In experiment (1) reflector tubes were used but the spaces between them were closely packed with asbestos board. In experiment (2) the reflector tubes and asbestos were removed entirely, and in experiment (3) the asbestos board of experiment (1) was replaced by tightly packed asbestos paper. The results of these three experiments thus give an idea of the efficiency of the thermal insulation. The difference

between the results of experiments (1) and (3) was due to the difficulty of packing the asbestos board which gave rise to the formation of gaps between the layers of the insulation material, and thus to increased convection and consequent heat-transfer loss.

Table 3

Experiment and details of thermal insulation. Pressure, 200 atmospheres	Temperature (°C.) at						Power required (kW.)
	centre of catalyst chamber	surface of converter					
		top		centre wall	bottom		
		cover	wall		cover	wall	
(1) Reflector tubes and asbestos board insulation. Hydrogen and hydrocarbons in insulation space	450	134	240	168	98	—	3·4
(2) No reflector tubes or lagging. Hydrogen and hydrocarbons in insulation space	320	116	186	208	100	—	4·4
(3) Reflector tubes restored and packed with asbestos paper. Hydrogen and hydrocarbons in insulation space	500	—	92	114	—	102	1·7
(4) (*a*) Magnesia and asbestos lagging instead of reflector tubes and asbestos paper. Pure hydrogen in insulation space. Non-process experiment	450	—	178	92	—	132	2·6
(*b*) As at 4(*a*) with hydrogen and hydrocarbons in insulation space. Process experiment	480	—	107	96	—	96	1·6

In experiment (4) the reflector tubes and asbestos paper were not used, and a heater made up similarly to an ordinary laboratory furnace was tried. Magnesia and asbestos packing was placed closely round the heater tube and retained in position by an outer casing which slid easily inside the converter, the small space between them being filled with asbestos paper. The shrinkage of the packing on drying necessitated a few preliminary heating runs after which the spaces formed were repacked.

Two experiments were made with this arrangement: 4(*a*) was a static run in which tar was not treated and 4(*b*) was a process run. The results show that there is very little to choose between this form of lagging and that used in experiment (3); they also indicate the greater thermal insulation value of gaseous hydrocarbons as compared with hydrogen.

The possibility of reducing heat-loss by using other gases in the thermal insulation space was also considered. Different gases in the same space and between the same temperature-limits at the same pressure will have different coefficients of convection heat-transfer which will not necessarily be in the same relative order as the conductivity coefficients. Approximate values can be found for relative convec-

tion heat-transfer at atmospheric pressures by the methods described by Fishenden and Saunders[3]. These data can also be used approximately for pressure-changes by using the indices obtained by Petavel([3], p. 109). By this method of calculation the relative values for heat-transfer by convection at a mean temperature of 260° C. and a pressure of 200 atmospheres were found to be much the same for hydrogen and nitrogen but considerably greater for carbon dioxide. The conductivities of these gases, on the other hand, at 260° C. are in the ratios 14 : 2·1 : 1·7 which are theoretically independent of pressure. Thus nitrogen and carbon dioxide have each a low conductivity while the conductivity of hydrogen is seven or eight times as great. If, therefore, convection could be excluded or reduced to a negligible amount, it would be worth while, if possible, to substitute for hydrogen in the insulation space some other gas of lower conductivity such as carbon dioxide or nitrogen, and so reduce the chief remaining source of heat-loss.

The thermal insulation value of different gases was tested in one of the converters of the larger type already described; the thermal insulation consisted of the reflector tubes and tightly packed asbestos paper. The experiments were made in the absence of the process, i.e. tar and hydrogen were not treated.

Carbon dioxide, having the lowest conductivity of the gases mentioned, was tested first. As there was no suitable pump available for transferring carbon dioxide to the converter at a pressure of 200 atmospheres, some preliminary experiments were conducted, (1) at atmospheric pressure and (2) at the maximum pressure obtainable with carbon dioxide from a cylinder. This pressure, at 450° C., was found to be 68 atmospheres.

Table 4

Gas	Pressure (atm.)	Internal temperature (°C.) at						
		top	7 in.	14 in.	21 in.	28 in.	35 in.	bottom
H_2	1	100	322	444	447	456	451	387
H_2	200	100	444	453	453	467	432	381
CO_2 65·8 per cent	1	98	353	449	451	456	450	346
CO_2 97·5 per cent	68	151	412	455	453	451	433	350

Gas	Pressure (atm.)	Surface temperature (°C.) at			Power (W.) at			
		top	middle	bottom	top	middle	bottom	total
H_2	1	58	73	60	415	403	338	1156
H_2	200	109	129	102	586	436	1240	2262
CO_2 65·8 per cent	1	38	43	38	272	182	206	660
CO_2 97·5 per cent	68	79	58	39	380	272	300 (?)	952 (?)

During the experiments, temperature-explorations were made in the thermocouple pocket in the centre of the catalyst bed, the object being to maintain this at 450° C. as closely as possible. Concurrently the surface temperatures of the outside of the converter and the power necessary on each of the heaters were recorded.

Experiments were made first with hydrogen at atmospheric pressure and at 200 atmospheres, then with carbon dioxide at atmospheric pressure and 68 atmospheres. It must be noted that the gas used in the first of these experiments contained only 65·8 per cent of carbon dioxide at atmospheric pressure, the remaining gas being chiefly carbon monoxide. At 68 atmospheres it contained 97·5 per cent of carbon dioxide; the reason for this is explained later. Table 4 gives the results of these experiments.

From this table it will be seen that the internal temperatures were in all cases maintained at about 450° C. The table shows moreover that the heat supplied and surface temperatures attained with hydrogen at 200 atmospheres were about double the corresponding figures at atmospheric pressure. It is also seen that at atmospheric pressure the impure carbon dioxide required about half the heat input required by hydrogen and gave much lower surface temperatures. The carbon dioxide at 68 atmospheres was better than hydrogen at one atmosphere and it is probable that this improvement would be maintained at 200 atmospheres and a saving of perhaps 40 per cent on power would be obtained. From the thermal point of view, therefore, the results were satisfactory, but difficulties of an entirely different nature, which are discussed later, arose.

Subsequently, four static runs were made to determine the thermal insulation value of nitrogen. The results are given in table 5.

These experiments show that the power requirements with nitrogen in the insulation space are only about 60 per cent of those with hydrogen. In practice, of course, the advantage of using a gas with an increased thermal insulation value would have to be balanced against the expense and complication entailed by the use of an additional gas.

Further experiments with nitrogen and hydrogen in the insulation space were again made with the design of converter (described on p. 343) in which the heater was wound directly on the catalyst chamber. The results recorded in table 6 show the thermal advantage of using this type of apparatus.

Temperature-control. The control of the reaction temperature is rendered difficult by the exothermic nature of the reaction and the relatively poor conductivity of the catalyst support. Heat may be generated more rapidly than it can be dispersed and since the rate of reaction rises with temperature, heat evolution may increase rapidly and cause a hot spot to develop. This excessive temperature leads to the deterioration of the catalyst and possibly to the deposition of carbon and ultimate coking of the catalyst.

Hence it is desirable to know as soon as possible of the presence of any excessive temperature and to take steps to correct it. For this reason, there were usually three thermocouples in the pocket in the centre of the catalyst chamber for indicating the temperature near the top, middle and bottom of the catalyst bed. The thermocouples were movable so that temperature explorations of the catalyst bed could be made from time to time.

The methods of temperature-control tried may be classified under three headings. (1) The use of several separate heaters to control the heat input to the

Table 5

Static experiments	Gas in insulation (per cent)	Temperature (°C.) in catalyst chamber at			Surface temperature (°C.) of converter at				Heater current (A.) at			Total power (kW.)
		top	middle	bottom	top cover	wall			top	middle	bottom	
						top	middle	bottom				
(1)	97 H_2	467	469	322	83	111	125	92	9·3	10·1	6·5	2·02
(2)	99·3 N_2	469	470	320	78	90	78	57	6·1	6·9	7·1	1·23
(3)	99·3 N_2	450	450	450	80	94	80	60	6·6	Nil	10·8	1·38
(4)	95·4 H_2 2·5 N_2	450	451	452	77	108	125	104	9·5	8·0	9·7	2·19

Table 6

Experiment	Gas	Catalyst temperature (°C.) at			Surface temperature (°C.) at				Heater current (A.) at			Total power (kW.)
		top	middle	bottom	top cover	wall			top	middle	bottom	
						top	middle	bottom				
(1)	H_2	290	460	460	85	95	100	85	7·5	6·7	7·6	1·27
(2)	N_2	294	459	478	90	92	58	39	6·5	5·8	4·5	0·77
(3)	N_2	282	456	482	76	75	52	37	6·0	5·6	4·5	0·70

chamber; (2) preheating of the entering tar and hydrogen before they reached the catalyst; (3) dissipation of the heat from incipient hot spots throughout the catalyst bed by means of metallic heat-conductors.

(1) Experiments with single heaters, whether uniformly wound or with graduated windings, showed them to have insufficient flexibility of control, and the standard system of three separately controlled heaters was soon introduced. It would be anticipated that the end of the catalyst chamber through which the cold tar and hydrogen enter would require most heat, this portion of the chamber serving to heat the materials to reaction point. In the form of heater used in all but the last experiments, however, this was not always the case, for the space between the heater tube and catalyst chamber permitted convection currents to carry the

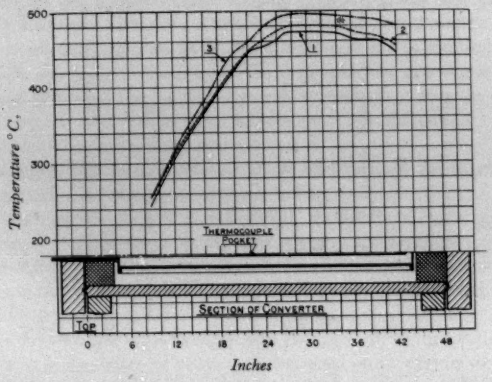

Figure 2.

heat supplied by the lower heaters to the top of the catalyst chamber. In some experiments, in fact, although most of the heat-loss took place at the upper part of the converter, it was found necessary to introduce nearly all the heat at the lowest heater. This is, of course, undesirable from the point of view of control of local heating and also involves running the heater wire at a much higher temperature than would be necessary if the heat were more uniformly distributed—a condition which increases heat-loss and, as will be shown later, is detrimental to the electrical insulation. This difficulty was largely overcome in the apparatus in which the catalyst chamber wound directly with the heating wire was used.

Typical temperature-exploration graphs of the wound catalyst chamber when running with the hydrogen in the insulation space are given in figure 2.

(2) In the catalyst chamber as normally arranged a considerable volume of catalyst near the inlet serves to bring the materials to reaction temperature. If it was attempted to maintain this region of temperatures in the neighbourhood of 450° C. by increasing the power on the corresponding heater, it was found that

coking of the tar usually ensued owing to the fact that the large flow of heat inwards and the poor conductivity of the catalyst bed caused considerable temperature-gradients and consequently excessive temperatures near the periphery of the bed. Attempts were therefore made to preheat the tar and hydrogen to a moderate degree, and with a smaller temperature-gradient, before they entered the catalyst bed.

A preheater at the upper end of the catalyst chamber was therefore designed and is shown in figure 3. This consisted of a cylindrical block of mild steel 8 in. long and 3 in. in diameter made so as to fit very tightly into the top of the reaction chamber. For the passage of the tar and hydrogen a U-shaped spiral groove $\frac{3}{16}$ in. deep and $\frac{3}{16}$ in. wide was cut in the surface of the block, the pitch being $\frac{1}{4}$ in. and the total length 25 ft. The tar and hydrogen passed via an internal channel to the beginning of the groove and similarly were led to the centre of the catalyst chamber at the other end. The top of this block was welded to the top of the catalyst chamber.

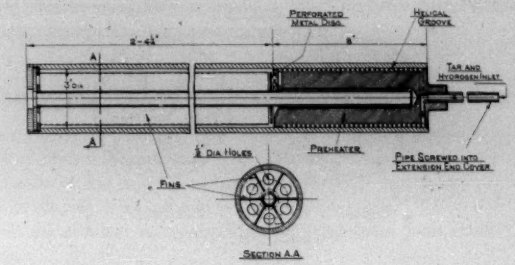

Figure 3.

During the first run with this arrangement, difficulties were experienced with excessive pressure-differences between the inlet and outlet of the spiral, and it was found that the spiral groove became filled with coke.

The spiral groove in the preheater was accordingly enlarged so as to be $\frac{7}{16}$ in. deep and $\frac{7}{16}$ in. wide with a pitch of $\frac{1}{2}$ in. and a total length of 12 ft. A few more or less satisfactory runs followed, in which pressure-differences were only noticed during the first few hours (i.e. while the plant was warming up). The experiments, however, were rather inconclusive as to the utility of this form of preheating although the indications were that this metal preheater offered no advantages over the catalyst bed.

Further experiments were made at a later stage. The catalyst chamber was extended by 2 in. and the top 7 in. of the chamber were filled with (i) pressed steel turnings and (ii) compressed steel wool. With these arrangements good temperature-control and temperature-distribution were obtained.

All experiments on temperature-control were subject to one peculiar difficulty; they were complicated by the fact that the skill of the operators played a large part, and much improvement in control as experiments proceeded was certainly due to the

increased skill of the operators. On the whole the results of the experiments with an internal metal preheater were not such as to justify its inclusion in the final form of apparatus.

(3) In order to disperse the heat arising from hot spots, the effect of placing good metallic conductors in the catalyst bed was tried. These took the form of six mild-steel strips of the same length as the catalyst chamber. These were disposed radially, and as far as possible were in contact with the outer wall. It was considered that this arrangement showed an improvement in ease of control and elimination of hot spots, and it was determined to carry the principle further to arrive at a more definite conclusion.

A new catalyst chamber shown in section in figure 4 was therefore constructed; it consisted of a mild steel cylinder 3 ft. 3 in. long and $3\frac{1}{2}$ in. in external diameter. Round the circumference were bored five longitudinal holes $1\frac{5}{16}$ in. in diameter to contain the catalyst and one central hole to accommodate the thermocouple pocket.

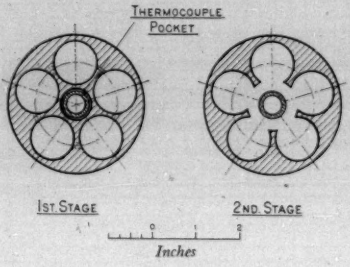

Figure 4.

The top of the cylinder was cup-shaped in order to facilitate the equal distribution of tar and hydrogen among the five tubes of catalyst. With the same end in view, horizontal holes were bored near the top of the tubes to provide intercommunication between them. The rate of flow of tar and hydrogen were reduced proportionately to the reduced amount of catalyst present.

The first run with this arrangement was difficult to control and on examination it was found that all the tubes had coked up over considerable portions of their length. It was concluded that there had been higher temperatures in the tubes than had been measured in the thermocouple pocket and that the tar-distribution between them had been irregular.

To minimize these difficulties the hole for the thermocouple pocket was bored out to a diameter of $1\frac{1}{8}$ in. so that it cut into the holes for the catalyst throughout its length, thus affording communication between them and yet leaving sufficient metal to improve the conductivity. The thermocouple pocket was fitted in position and the space around was filled with catalyst. A run lasting seven days was made with this chamber, during which there was little difficulty in control and little trouble from hot spots. Temperature-explorations showed that a large part of the

catalyst bed was at a uniform reaction temperature. This experiment proved that the increased metallic conduction provided had been of real value and confirmed the conclusion drawn from experiments with metallic strips.

The occupation of space by metallic conductors reduces the volume of catalyst and so reduces the throughput of raw material, and it becomes a matter of judgment how far it is worth while to carry the principle of improving conductivity in this way. In this connexion it must be borne in mind that with a grain-size of catalyst-support of about $\frac{1}{8}$ to $\frac{1}{4}$ in. the interspaces are so large that under the conditions of high pressure and considerable temperature-gradient the convection is probably more important than the conduction of heat. This has been shown in connexion with the experiments on thermal lagging. The introduction of metallic conductors, although improving conduction, may to some extent restrict lateral convection currents, and it is perhaps due to this that the advantage of using the fins was not as great as had been anticipated. To improve the dissemination of heat by convection would involve using large grain-sizes. This, however, is undesirable as the catalyst in larger grain-sizes deteriorates more rapidly.

§ 4. PROBLEMS RELATING TO ELECTRICAL INSULATION

From the electrical point of view the chief difficulty encountered was the maintenance of electrical insulation between the heating elements and earth, and between the coils of the heating elements. Difficulties were materially increased by the fact that the only source of power available was a 220-V. d.-c. supply. There is no doubt that one of lower voltage and isolated from other plant would have been an advantage.

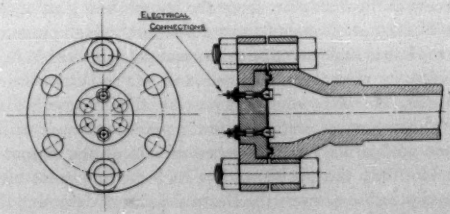

Figure 5.

The electrodes carrying the currents were brought into the converter through the cover by steel rods which passed through conical red fibre bushes as shown in figure 5. Red fibre has so far shown itself to be the most satisfactory substance for this purpose and can be used up to temperatures of 150° C. Most other substances are too rigid or too plastic at such high temperatures to remain tight at a pressure of 200 atmospheres, but other materials have been and are being investigated with a view to their substitution in certain cases. Inside the converter the steel rods were encased in silica or pyrex glass tubes surrounded by asbestos packing. In the earlier

experiments, when the wall temperature of the converter was high, extension pockets which could be water-cooled and whose ends carried the red fibre joints were used. Trouble was, however, experienced owing to the condensation of moisture on the terminals. A diagram of one of these extension pockets is shown in figure 5.

In the first experiments the elements of the heater were wound on a silica tube. This, however, was usually found cracked and broken after two or three runs, and on one occasion was disintegrated into small fragments which were found to be slightly explosive, a property they retained for over a year. The phenomenon was evidently due to the occlusion of hydrogen in the silica at high temperatures and pressures, the permeability of silica to gases increasing rapidly at high temperatures.

The heating elements were thereafter wound on an iron tube and insulation was effected by means of a layer of mica held between two sheets of asbestos paper on the outer of which the wire was wound. The spaces between the turns of wire was usually filled with a fireclay cement.

In the first form of apparatus an attempt was made to preheat the hydrogen before it joined the tar by circulating it through the thermal insulation space. With this apparatus trouble was experienced in maintaining the electrical insulation, and certain mechanical difficulties arose; this attempt to preheat the hydrogen was accordingly abandoned and simpler forms of apparatus such as those already described were adopted. It was found very difficult, however, to maintain the electrical insulation owing to the deposition of moisture on the electrodes inside the converter. This moisture was derived by distillation of hygroscopic moisture from the hotter parts of the asbestos lagging and from asbestos, such as that under the heater, raised to 600° C., at which temperature water of constitution is given off to the extent of about 15 per cent. In those experiments in which the products of reaction had access to the insulation space the trouble was greater, as water is one of the products of reaction. It must be noted that, at the high pressures used, water will distil from the hotter regions to the colder and deposit there in liquid form at all temperatures below its critical temperature, and as the electrodes, on account of the red fibre bushes, were kept as cool as possible they received this condensation very markedly. This was noted in the first few experiments made with the converter with an extension pocket; the trouble was eventually greatly reduced in that form of construction by filling the pocket with a high-melting-point bitumen. Later, when it was found possible to insert the electrodes directly through the lower cover of the converter, the trouble again became acute as the water collected in the bottom. The insulation was again restored by making wider holes on the inside surface of the cover where the electrodes passed through it (the fibre bush being at the bottom of the holes) and filling them with a non-volatile hydrogenated tar oil whose density was greater than that of water up to 100° C. These methods, while effective within limits, were only palliations. A more direct method was to dry out the lagging before each run by heating up the converter and exhausting the insulation space containing the lagging. The amount of water abstracted in this way was remarkably high and the insulation obtained was good. In these experiments, however, in which the products of reaction had access to the insulation space, the

electrical insulation would again gradually fall until it was only a few thousand ohms. When this space was swept out by means of pure dry hydrogen, and so re-evaporating the water formed, the insulation was usually restored to some extent. In the later forms of construction, where the catalyst chamber was not in connexion with the insulation space and the latter was filled with hydrogen or nitrogen, trouble due to the deposition of moisture was eliminated if the converter was dried out *in vacuo* before the run.

As regards the insulation of the heating element itself, moisture could not be deposited, the temperature being too high. The first trouble with the heater occurred through deposition of carbon on its surface and in the insulation material under and between the wires. This occurred sometimes in runs in which the hydrocarbon vapours from the reaction had access to the insulation space, when, if the temperature of the wire was high, cracking of some of these vapours would ensue in spite of the excess of hydrogen. This was markedly shown in some experiments in which the top heaters, which were hottest, became earthed owing to carbon deposit. This form of trouble was also eliminated when designs were adopted in which the outer space was filled with pure nitrogen or hydrogen.

During experiments for determining the thermal insulating properties of different gases, a similar difficulty in maintaining electrical insulation was experienced when carbon dioxide was used. This difficulty, which led to the abandonment of carbon dioxide, is perhaps of sufficient interest to be described at some length.

The heater and insulation material used in the experiments were new and uncontaminated, although the catalyst chamber had been used previously and was coated with a film of ferrous sulphide. The converter was first dried out by heating *in vacuo*, and then the experiments with hydrogen were carried out. The converter was again evacuated, and the experiments with carbon dioxide were carried out. During these experiments, insulation trouble developed and in the last experiment with carbon dioxide at high pressure the insulation of all heaters decreased seriously. The line conductivity of the lower element greatly increased, allowing a large current to flow and making the power-measurement on this heater uncertain—hence the query in table 4. The carbon dioxide from the cylinder was 98·5-per-cent pure, but when a sample was drawn from the converter during the course of the experiment at atmospheric pressure it was found to have the following composition: CO_2, 66; CO, 28; and H_2, 6 per cent. Repeated experiments gave the same result. In the high-pressure experiments, on the other hand, the purity of the original carbon dioxide had only fallen very slightly from its value of 98·5 per cent after many hours heating.

The explanation of these phenomena is probably given by the following equilibrium:

$$3Fe+4CO_2 \rightleftharpoons Fe_3O_4+4CO.$$

The presence of carbon monoxide suggested the possibility of iron carbonyl being formed under certain conditions and subsequently decomposed. It is probable that iron carbonyl was formed in the regions where the temperature was most favourable and diffused to the heater, where it was decomposed and iron was

deposited between the turns of the winding and between the winding and tube, leading to partial short-circuiting. On cooling, the iron again largely recombined to form iron carbonyl and the insulation improved. This would also explain the observed increase of insulation and of conductivity resistance which took place when the heater cooled.

This explanation was confirmed after the experiment when iron was found in the insulating material in the neighbourhood of the wire of the heater. Some Fe_3O_4 was also found on the surface of the catalyst chamber after these runs. It is probable that the hydrogen found was desorbed from the steel which had been subjected to high hydrogen-pressure.

For all early experiments the heater tube itself had not been insulated from the converter; in later experiments a great improvement in the insulation of the heaters from earth was effected by interposing a block of sindanyo between the tube and the legs connecting it to the converter. This was found to increase the electrical insulation from 40 MΩ. at room-temperature and 3 MΩ. at 450° C. to nearly double these values. By this means it was found possible to make long runs in which the insulation was maintained at values of the order of 100,000 Ω., but it was found that there were other factors the consideration of which could lead to further improvement.

It had been noted on many occasions that rise of temperature of the heaters was accompanied by a great fall in electrical insulation, whatever the pressure of the gas in the thermal insulation space. This might be of the order, *in vacuo*, of 80 MΩ. at atmospheric temperature to 4 MΩ. at a temperature of 400° C. in the catalyst chamber, which is lower than the running temperature of the wires. If an abnormally high current was carried by one of the elements, still lower values were obtained.

This result was at first attributed entirely to the rapid decline in insulating power of such materials as mica and asbestos as they are raised in temperature, and there is no doubt that this was largely the cause. There were, however, other observations to show that a further cause was probably operating. Apart from the temperature effects above referred to, the observations were that insulation (*a*) was not so good *in vacuo* as when a gas was present; (*b*) was not so good in hydrogen as in nitrogen or air; (*c*) was not so good at low as at high pressures. These observations led to the conclusion that it was probable that thermionic emission from the heater wires was at least partly responsible for the fall of insulation, as a comparison with the known facts concerning thermionic emission shows. Thus, emission increases very rapidly with rise of temperature, and is greater when the emitter contains occluded gas. In addition, ionic mobilities are greater *in vacuo* and in gas at low pressures than in gas at high pressures, and are greater in hydrogen than in nitrogen.

In the design of the last arrangement, in which the heating wire was wound directly on the catalyst chamber, the latter could not be insulated from the rest of the converter. The thickness of the mica insulation on which the heaters were wound was therefore increased from $\frac{1}{32}$ to $\frac{1}{16}$ in. to compensate in some degree for this. In the runs with this converter, it has already been shown that owing to the direct application of the heat (*a*) the currents were small and the temperatures

of the wires lower than usual and (*b*) no wire carried an excessive proportion of current. The result of this was that the best values of electrical insulation maintained during a continuous experiment were secured. The insulation of the system started at 100 MΩ. at atmospheric temperature and was found under running conditions not to fall below 0·25 MΩ. with hydrogen or 2·0 MΩ. with nitrogen.

§ 5. ACKNOWLEDGMENTS

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THE BEHAVIOUR OF A SINGLE-HAIR HYGROMETER UNDER VARYING CONDITIONS OF TEMPERATURE AND HUMIDITY

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ABSTRACT. A sensitive single-hair hygrometer is described which enables observations to be carried out, over an extended range, on the effects due to variations in relative humidity and in temperature. The temperature coefficient of a stretched hair in an atmosphere kept at a relative humidity of 100 per cent is negative for temperatures above about 1·5° C. and positive in the range below that temperature. If the hygrometer is kept at a constant temperature and the relative humidity of the air is decreased from 100 per cent there is an immediate increase in length, corresponding to an apparent increase in relative humidity of about 3 per cent, followed by a contraction to the equilibrium length characteristic of the lower humidity. It seems probable that this effect may account for the apparent supersaturation sometimes seen in balloon meteorograph records. With this hygrometer the scale value for relative humidity was dependent on temperature. The lag in response of the single hair varied with experimental conditions, and was often considerable. It will have its maximum effect when humidity is varying rapidly as in a rising balloon, but will be of much less importance with hair hygrometers used on the ground, since there conditions alter relatively slowly, and the hair will always be in approximate equilibrium with the air surrounding it.

§ 1. INTRODUCTION

Balloon meteorograph records obtained with a hair hygrometer[1] appear to indicate in certain cases conditions of supersaturation in the upper atmosphere[2]. The records shown in figure 1, kindly supplied by Mr Dines, show this effect at 0·7 and 2·7 km. on the ascent and again at 0·9 and 2·2 km. on the descent. As it is difficult to picture the conditions under which supersaturation would occur, we decided to carry out some experiments to ascertain whether the effect could be produced under controlled conditions in an atmosphere at a relative humidity of not more than 100 per cent.

The length of a stretched hair in a moist atmosphere is a measure of the relative humidity of that atmosphere. The equilibrium between hair and atmosphere must be dynamic, as many molecules of water leaving the hair as arrive and are absorbed; equilibrium takes a finite time to be established. There is no experimental evidence to show that a hair can absorb more water than it does in a saturated atmosphere. Actually it is usually assumed by meteorologists that a hair immersed in water

registers a relative humidity of only about 95 per cent, when its length in saturated air is taken to be equivalent to a relative humidity of 100 per cent, though one might perhaps expect an increase in length under these conditions. But the surface conditions are very different for a hair immersed in water and for one in a saturated atmosphere, and it is possible that an increase in the vapour-content of air already saturated would cause the hair to absorb more water molecules and so increase in length. It is also possible that a change in temperature at constant relative humidity

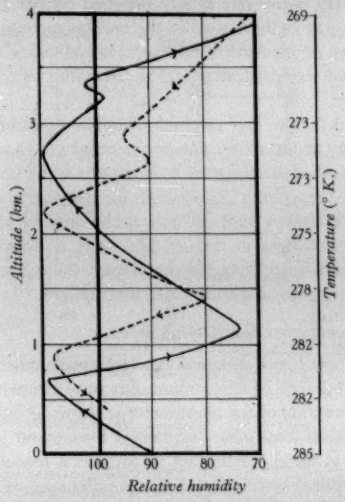

Figure 1. Balloon meteorograph record. The full curve is the record obtained while the balloon was ascending, the dotted curve while descending. The saturation line shown is that obtained by immersing the hair in water. This is usually taken to represent a relative humidity of only about 95 per cent.

might temporarily alter the equilibrium in such a way as, for instance, to decrease the rate of loss of water while maintaining the absorption-rate constant, and so produce an increase in length suggesting supersaturation.

Some rough qualitative experiments made with a recording hair hygrometer kindly lent by the Meteorological Office, and with a single hair hygrometer, showed that a fall in temperature from 15° C. to 0° C. at a constant relative humidity of 100 per cent did, when temperature and length had again reached equilibrium, produce an increase in length. This negative temperature coefficient is in agreement with the results of Griffiths[3] and Pfeiffer[4] but contrary to those obtained by Grundmann[5].

The experiments also showed that a hair maintained for a considerable time at a relative humidity of 100 per cent developed a certain plasticity, and that its

readings were not quantitatively reproducible. We found that even more irregular behaviour resulted from a complete drying of the hair. In later experiments we were careful, therefore, to avoid leaving the hair for many hours in a very wet or dry atmosphere; for this reason air at room humidity was drawn into the hair-chamber at the end of a day's run.

The human hairs used were prepared by soaking in ether, carbon tetrachloride or alcohol, but the method of preparation had no apparent effect on the behaviour of the hair. Five of the hairs were kindly supplied by Mr Dines, and had been prepared in the same way as those used in the balloon meteorograph. Only one of these hairs (no. 4) received any further treatment; it was soaked in ether for 24 hours, and washed in distilled water before use. The behaviour of this hair was identical with that of the others.

The time required for the hair to reach complete equilibrium when the temperature was varied by about 10° C. was of the order of 1 hour, and a similar lag has been observed by other investigators.* It appears to be impossible to maintain supersaturation in an atmosphere long enough for the hair to attain even approximate equilibrium. Temporary supersaturation can only be attained by processes involving temperature-changes in the air, and as it is desirable to separate the effects due to alterations in relative humidity from those due to temperature we made no attempt to work in a supersaturated atmosphere.

§2. APPARATUS

The apparatus adopted was designed to allow measurements of the change in length of the hair with change of relative humidity or of temperature, in stagnant or flowing air. The construction of the hygrometer is shown in figure 2*a*. The hair *H* is mounted on a stainless steel pillar, supported by a stand with three levelling-screws, and carrying at the top a bracket to support a loaded optical lever. The arrangement of the optical lever allowed the maintenance of a sensibly constant tension of 1·5 g. on the hair, permitted the maximum angular deflection to be read, and was easy to adjust for zero. This is the load used in the balloon hygrometers, but is three times as great as that employed in the recent work of Grundmann[5]. The pivot of the mirror was a roller of stainless steel, and worked very smoothly. The movement of the mirror was observed by means of a telescope and scale, combined with a reflecting prism.

The hygrometer was contained in the refrigerating chamber shown in figure 2*b*. This was in the form of a cylindrical tube of internal diameter 7 cm., whose walls were formed by a spiral coil made of copper tubing $\frac{3}{8}$ in. in diameter, wound closely and soldered solid on the outside, to give an airtight vessel with a capacity of about half a litre. This gave very efficient cooling inside the chamber, when cold alcohol was circulated by a gear pump through the spiral, because of the large area of cold metal in contact with the air. The base was formed by a brass disc *A*, to which was soldered a brass tube fitting inside the lower portion of the copper spiral. This was supported on three glass tubes *G*, 1 in. long, and was clamped to a piece of slate *B*

* See for instance Griffiths[3].

by brass screws, one passing down the axis of each glass tube. This slate was supported on four pieces of cork, and clamped to the slate bench by a single bolt *C*. This arrangement ensured a rigid support, while providing good thermal insulation when the whole was packed in slag wool. The experimental chamber had an inner base *L*, which supported the hygrometer, and stood above a shallow vessel in which could be placed water, or a solution of known vapour pressure. The presence of

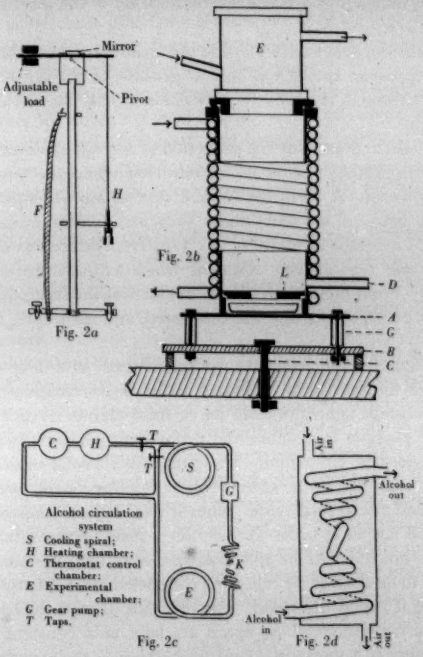

Figure 2.

liquid in stagnant air maintained the relative humidity at a constant value but it took a long time to attain equilibrium in the vessel when the temperature was changed. To aid the establishment of equilibrium a piece of filter paper *F*, figure 2*a*, dipped into the water and was held parallel and close to the hair by two clips on the stainless steel pillar.

This experimental chamber could also be used with flowing air. In this case conditions more closely resemble those in which the balloon records were obtained. Inlet and outlet tubes (not shown in figure 2*a*) were inserted so that air of known humidity could be admitted at the top and flow out through the base. The dish of

liquid placed in the chamber for the stagnant air experiments was, of course, removed.

The mirror of the hygrometer was observed through the top of the cooling-chamber, which was closed by the vessel *E*, made of two parallel glass plates, separated by a jacket through which dry air was circulated. This vessel screwed into the top of the chamber, and an air-tight joint was made by a rubber washer. This arrangement was adopted to prevent the obscuration of the glass by moisture, and proved quite satisfactory.

There were three thermocouples inside the chamber, one in the water, one near the wall of the chamber, and one as near as possible to the centre of the hair, the leads coming out through the tube *D*. It was found that they all showed the same final temperature.

A test was made to determine the deflection of the optical lever due to the contraction of the supporting system which occurred when the temperature of the apparatus was lowered. A phosphor-bronze wire of known expansion coefficient was mounted in place of the hair, under sufficient tension to keep it taut, and allowed to attain a constant length at 15° C. The temperature was then lowered and the change in scale reading was observed when temperature and length again became constant. From these observations the shift of the beam of light due to the change in length of the steel pillar was calculated, and all graphs are corrected for this effect.

The experimental chamber could be maintained at a low temperature by pumping through the tubular wall alcohol cooled by circulation through a spiral tube kept at a constant temperature in ice or solid carbon dioxide. It was hoped that it would be possible to produce any desired temperature in the chamber by controlling the speed of circulation. However, the thermal insulation proved so efficient that any alteration in the speed of pumping merely changed the rate of fall of temperature, and not its final value. Since it was obviously necessary to have the whole system well lagged in order to maintain a steady temperature, independent of room temperature fluctuations and draughts, over long periods, the control of temperature had to be effected by reheating the cooled alcohol to any desired extent before circulating it round the vessel. For this purpose the alcohol was passed in turn through the cooling spiral *S*, figure 2*c*, kept at a constant temperature, a heating-coil chamber *H*, a thermostat control chamber *C*, the experimental chamber *E*, a coil *K* to be described later, a gear pump *G*, and back to the cooling spiral.

The thermostat operated a hot-wire mercury-switch relay in a circuit containing a two-way switch. In one position the two-way switch allowed current to pass continuously through one half of the heating-coil, which was centre-tapped, and through the other half when the thermostat control permitted. In the other position the current was completely controlled by the thermostat.

The gear-pump casing was made of ebonite, in order to provide good thermal insulation. The pump was driven through a reduction worm and pinion gear of about 56 to 1. The pump and motor were mounted on a heavy iron pillar which rested on four pieces of soft rubber; this gave satisfactory insulation against any

mechanical vibration which might have been transmitted through the block floor and bench to the optical lever. The speed of the motor could be controlled, and was measured by the reading of a suitably calibrated ammeter.

To produce a steady flow of air at any desired relative humidity the humidity-controller of Walker and Ernst was used[6]. In this apparatus a blower produces two streams of air, one of which bubbles through water at a known temperature and becomes saturated, while the other passes over various dehydrating agents. The wet and dry air-streams pass through separate flow-meters, and hence to a vessel where they mix in the proportions indicated by the flow-meters; the mixture is admitted to the apparatus through a third flow-meter.

It was found that, in the arrangement of Walker and Ernst, condensation occurred in the tubes by which the saturated air, which was originally above room temperature, reached the mixing vessel, and hence the relative humidity of the mixture was less than the calculated value. Lagging these tubes was found unsatisfactory. The apparatus was therefore rearranged so that the whole of the path of the wet air and the mixing vessel were contained in the same thermostat as the vessel in which the air became saturated. Although accuracy greater than ± 5 per cent is not claimed, at relative humidities less than 100 per cent, it was always possible to produce a flow of air accurately known to be at a relative humidity of 100 per cent, as the temperature of the thermostat was higher than that of the experimental chamber.

To achieve temperature equality between the hygrometer and the inflowing air, a brass cylinder *K*, figure 2*d*, containing a copper spiral in the form of a double cone, was packed near the experimental chamber, and the cold alcohol circulating round the walls of the latter was passed through this spiral. Air at a known relative humidity and at the temperature of the thermostat entered the cylinder, passed over this spiral cooling-coil, and so attained the temperature of the experimental vessel before reaching the hygrometer. The rate of flow of air through the hygrometer vessel was about 1 litre/min. Tests showed that this temperature-equalization of experimental chamber and inflowing air was perfectly satisfactory, and a knowledge of the initial relative humidity of the inflow and its initial and final temperatures allowed the relative humidity of the air reaching the hygrometer to be calculated.

§3. RESULTS

Using the apparatus described we have measured the variations in length of the hairs under the following conditions. (i) Relative humidity maintained at 100 per cent, temperature lowered quickly, with stagnant and flowing air; (ii) relative humidity maintained at 78 per cent and at 88 per cent, temperature lowered quickly, with stagnant air only; (iii) temperature kept constant, relative humidity decreased quickly from 100 per cent, with flow method only; (iv) temperature kept constant, relative humidity decreased quickly from a value less than 100 per cent, with flow method only; (v) we have also measured the percentage change in length due to a known variation in relative humidity for a series of temperatures by the flow method.

With the exception of (ii) each of the above experiments was made with two or

three different hairs, and the hairs were prepared by different methods. In all cases the behaviour was identical, although numerical agreement was not obtained.

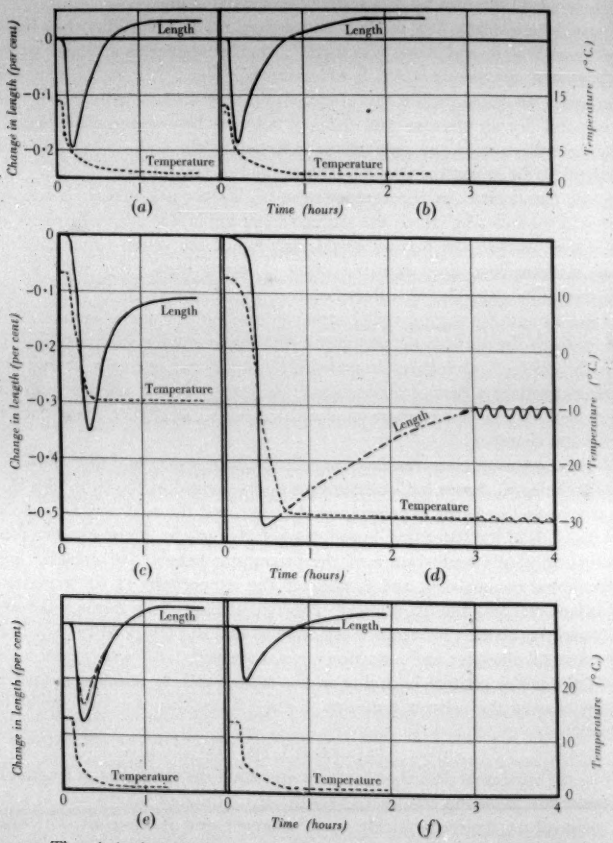

Figure 3. The relative humidity is 100 per cent for (*a*), (*b*), (*c*), (*d*), (*e*) and 78 per cent for (*f*). The stagnant method was used for (*b*) and (*d*) and the flow method for (*a*), (*c*) and (*e*).

Typical graphs for case (i) are given in figure 3, the dotted line showing the temperature-change with time.

Both the stagnant and flow methods gave similar results as the hair cooled, but its equilibrium length was rather more quickly attained in the latter method. In all cases the immediate effect of a fall in temperature was a *decrease* in length of the

hair, a minimum length being reached before the thermocouple in the hygrometer chamber became steady. The time required to attain temperature-equilibrium was from 20 to 45 min., though by far the greater part of the fall in temperature had in all cases occurred in 10 min. After this preliminary contraction the hair expanded, reaching a final equilibrium length after from 1 to 3 hours, though most of the change in length had occurred by the end of half an hour.

This initial rapid contraction of the hair appears to be due to experimental conditions. The sudden cooling of the wall of the vessel lowers the water-vapour pressure near it, and the pressure-gradient so set up causes vapour to diffuse out from the centre. There will therefore be an immediate drop in relative humidity near the hair corresponding to its initial rapid response. Temperature-equilibrium on the other hand takes some time to be established, and it is possible to estimate the relative speeds of the two effects. A rough calculation shows that temperature-equalization will occur considerably later than the disappearance of the vapour-pressure gradient.

The hair has completed its contraction and commenced to expand after about 6 min., and by this time the vapour pressure should be uniform throughout the vessel. Owing to the normal lag in response of the hair the final length will not be attained for about an hour, and by this time temperature-equilibrium is achieved.

The fluctuations appearing in the temperature line of figure 3*d* support this explanation. The variations are about 1° C. and are due to the switching on and off of the heating-current owing to unsatisfactory setting of the thermostat contacts. The other curve in figure 3*d* shows variations in the length of the hair of about 0·01 per cent, approximately synchronizing with the temperature variations. Two or three curves of this nature were obtained. In the case of flowing air there were some irregularities in the fluctuations of temperature and therefore of length. Hence it was possible to distinguish corresponding peaks in the temperature and length graphs, and it was found that the length-variation lagged behind the temperature-change by about 4 min.

Figures 3*a*, 3*b*, 3*e* and 3*f* all show a final length greater than the initial, while in figures 3*c* and 3*d* the hair is shorter than at the commencement. In figure 3*d* the rise to the final steady value is indicated by a dotted line, since the points on the ascending portion of the graph were scattered owing to the fluctuations of temperature mentioned above. These occurred throughout the run, after the initial sudden temperature-drop, but are only indicated on the figure during the equilibrium period of the hair.

It was thought that the initial drop in relative humidity near the hair was assisted by the presence of dust acting as condensation nuclei. A filter consisting of a glass tube 12 in. long, $2\frac{1}{2}$ in. in diameter, and packed with wool, was inserted in the air circuit to remove dust. Since the wool was hygroscopic the filter had to be placed in the air intake, and so did not remove any drops carried in the airflow. The result, shown in a broken line in figure 3*e*, was a decrease in the amount of the initial contraction, probably due to the reduction in the number of condensation nuclei by the removal of dust.

Expansion coefficient. Figure 3 shows that the final length of a stretched hair cooled from room-temperature may be either greater or less than its original value, the equilibrium length attained depending only on the final temperature. In figure 4 are shown the results of cooling the same hair in a saturated atmosphere to several final temperatures. The change in length of the hair is expressed as a percentage of its length at the initial temperature of 16° C. and is plotted against the final steady temperature attained. In all cases the hair was in equilibrium with the moist air before cooling commenced, and was left long enough to attain a constant length after cooling. We found that the final length attained by the hair was a true equilibrium value since it was the same whether it was cooled from, say, room-temperature to −10° C., or cooled from room-temperature to 0° C., allowed to reach equilibrium at 0° C., and then cooled to −10° C.

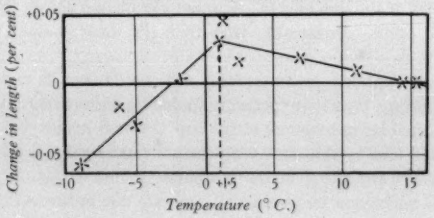

Figure 4. Variation of length of hair with temperature when relative humidity is 100 per cent.

The coefficient of expansion of a hair in a saturated atmosphere changes sign at about 1·5° C. It is negative for the range from 20° C. down to 1·5° C., but for temperatures lower than 1·5° C. it has a positive value, so that a hair maintained at a relative humidity of 100 per cent and initially at 1·5° C. will show a final decrease in length when either heated or cooled.

The coefficients of expansion on either side of 1·5° C. are approximately constant over the range investigated. Down to 1·5° C. the values obtained for two typical hairs were $-2{\cdot}3\times10^{-5}$ and $-1{\cdot}9\times10^{-5}$, and for lower temperatures $+9{\cdot}9\times10^{-5}$ and $+14{\cdot}6\times10^{-5}$ per unit length per °C. Figure 4 shows that the hair, no. 5, cooled from 16° C. attained its original length at −3° C., but the temperatures at which the lengths are the same will vary from hair to hair owing to variations in temperature coefficient.

The temperature at which the length is a maximum cannot be fixed with precision though it seems to be the same within 1 or 2° C. for all hairs investigated, and to be above 0° C. It is possible that at the inversion temperature some change of state of the absorbed water occurs with change in its vapour pressure and in its actual volume. It is difficult to say what would be the freezing-point of the absorbed water.

These results account for the discrepancies in expansion coefficient obtained by various observers and referred to above; for the value obtained will vary with the temperature-limits if the temperature-range passes through 1·5° C.

We conclude that temperature-variation will have only a small effect on the balloon hygrometer records, for the instrument will in this case be moving rapidly through a temperature-gradient, and through layers of varying relative humidity. Though it will not have time to reach equilibrium in any particular layer, its reading will, unless the relative humidity varies very considerably, approximate to the correct relative humidity for the corresponding height recorded by the barograph. There will be no deflection corresponding to the initial decrease in length observed in our experiments, since there will be no conditions occurring which correspond to those

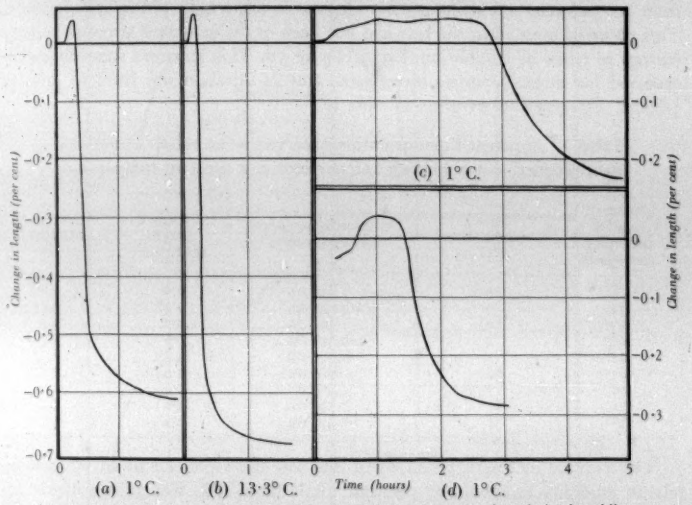

Figure 5. Apparent supersaturations produced on lowering the relative humidity from 100 per cent.

causing the vapour pressure gradient in the experimental chamber. The correction due to the temperature coefficient will probably be small compared with the error due to the lag of the instrument.

In case (ii) the relative humidity was constant at 78 and 88 per cent and the temperature was lowered quickly. A saturated solution of sodium or of potassium chloride was placed in the dish in the hygrometer vessel, so that the relative humidity of the stagnant air above it was maintained at the corresponding maximum vapour pressures of 78 and 88 per cent respectively. The saturation vapour pressure of these solutions varies only about 2 per cent over the range of temperature 12° to 0° C., and thus it was possible to observe the effect of change of temperature when the relative humidity was maintained approximately constant at a value less than 100 per cent. The initial result of lowering the temperature was, as at a relative humidity of 100 per cent, an immediate contraction of the hair, figure 3*f*. It

therefore appears that a drop in relative humidity due to the vapour-pressure gradient occurs in this case also. The temperature coefficient at these lower humidities had the same sign and approximately the same value as at a relative humidity of 100 per cent, though the investigation was not in this case carried below 0° C.

(iii) In the case where the temperature was constant and the relative humidity decreased from 100 per cent the following observations were made.

The apparent supersaturation. Experiments were carried out in the flow apparatus, and in every case the initial result of decreasing the relative humidity from 100 per cent was an immediate increase in the length of the hair, figure 5. This occurred even when the hair had not been in the saturated atmosphere long enough to attain its equilibrium length, figure 5*d*. This apparent supersaturation occurred for all temperatures investigated and its duration was from 10 min. to 3 hours. Observations are given in table 1.

Table 1. Apparent supersaturation observed when relative humidity was decreased suddenly from 100 per cent at a constant temperature

Change in relative humidity (per cent)	Steady temperature (°C.)	Duration of apparent supersaturation	Change in length (per cent)	Reference number of hair
18	12·8	40 m.	0·2	4
34	1	2 h. 40 m.	0·38	4
37	12	40 m.	0·2	4
46	1	1 h. 40 m.	—	3
47	1	1 h. 15 m.	0·25	2
63	12	10 m.	0·45	2
66	1	15 m.	0·4	2
71	1	40 m.	0·1	3
76	1	40 m.	0·2	4

The increase in length produced in this way corresponded to an increase in relative humidity to about 103 per cent. It is impossible that such a degree of supersaturation could even momentarily exist in the experimental chamber as condensation nuclei were present in great numbers, the air flowing into the chamber was subject to only a negligible pressure-drop and there could be no appreciable adiabatic cooling. It appears therefore that it cannot be a true supersaturation of the air that is indicated by this extension.

If water vapour had condensed on the hair, reduction of humidity would cause it to evaporate, thus producing a temporary fall in temperature. In the neighbourhood of 10° C. this would cause an expansion, but an expansion of the observed magnitude would require a cooling due to evaporation of about 10° C. Also the expansion is still observed at a temperature of 1° C. although the temperature coefficient predicts a contraction with fall of temperature. It is therefore difficult to explain the initial expansion in terms of a temperature-drop due to evaporation, although, as will be seen below, the effect is only observed when the initial relative humidity is 100 per cent, and is therefore probably connected with the presence of drops of water on the hair.

It is even more difficult to account for the widely different durations of the apparent supersaturations under similar conditions. The graph in figure 5*c* shows the longest time for which it was observed. In those cases where the apparent supersaturation lasted a long time the final contraction of the hair to its equilibrium length at the lower humidity was more gradual than when it lasted only about 10 min.

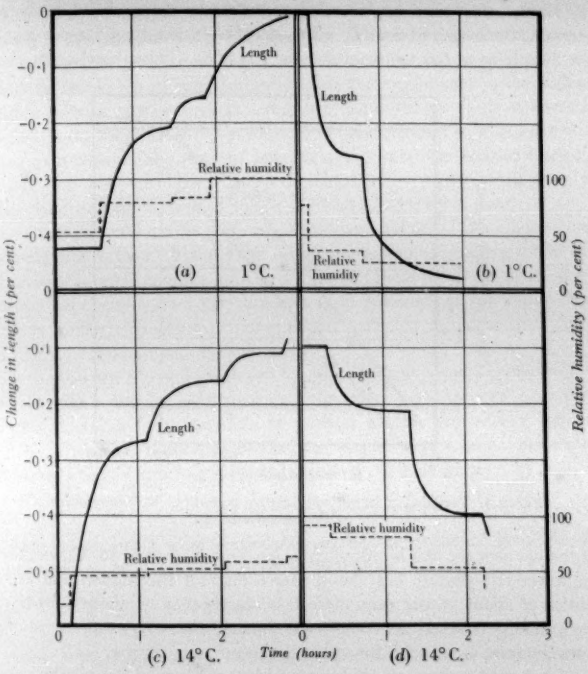

Figure 6.

The initial treatment of the hair does not appear to account for the variation in duration, since two hairs prepared in the same way, and subject to humidity-change at the same temperature, showed supersaturation lasting for 15 min. and 1¼ hours. There are at least two influences acting on the hair, one being the normal loss of water from its cells leading to a contraction, the other connected probably with the evaporation of drops of water from its surface. The latter effect is presumably the more immediate and may account for the fluctuations in length following the switching on and off of the thermostat, as shown in figure 3*d*.

(iv) When the temperature was constant and the relative humidity varied from values less than 100 per cent, figures 6*a* to 6*d*, in every case the length of the hair

followed the change in humidity with a considerable time lag. Equilibrium was reached in times varying from 20 min. to 1 hour, the lag being greater for large changes in humidity. *There was no indication of the initial expansion which occurred when the initial relative humidity was 100 per cent.* The time lag appeared to be about the same at all temperatures for a given drop in humidity.

(v) From curves similar to those discussed under (iii) and (iv), it was possible to determine the length of the hair with respect to its length at 100 per cent for any relative humidity at the temperatures 16° and 1° C. These results are plotted in figure 7.

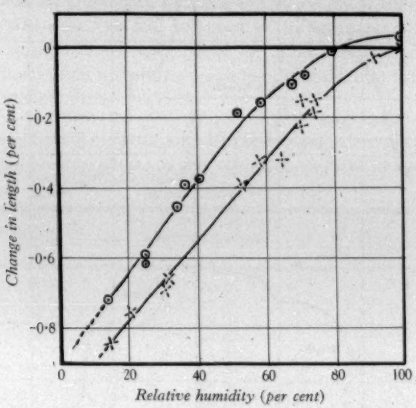

Figure 7. Variation of length with relative humidity. ⊙ Temperature 0° C.; × Temperature 16° C.

At 100 per cent the hair is only slightly longer at 1° than at 16° C., but the curve for the lower temperature lies always above that for the higher, and at relative humidities of about 50 per cent there is a discrepancy of about 15 per cent in relative humidity between the two curves, showing that a hygrometer calibrated at room-temperature is unsuited for use at the lower temperature.

It is interesting to compare this result with the theory of Sresnevsky quoted by Whipple[7]. He considers the negative pressure Q developed in a cell partially filled with liquid, i.e. the intra-molecular spaces in the hair, and obtains the formula

$$Q = R\rho\theta \log_e\left(\frac{p_0}{p_1}\right) - P_0,$$

where ρ is the density of the liquid, θ the absolute temperature, p_0 the saturation vapour pressure at temperature θ, p_1 the vapour pressure in the cell, and P_0 atmospheric pressure.

Hence the force causing the hair to contract is proportional to the absolute temperature and inversely proportional to the relative humidity. For a range of temperature down to 1·5° C. the change in length with temperature at constant

relative humidity, which we observed, is in the direction predicted by this theory. The theory however does not agree with experiment at lower temperatures, and there are apparently other processes taking place which a satisfactory theory would have to allow for.

The results of these laboratory experiments show that when a hair is in saturated air, and when the humidity of this air is reduced, an increase in length of the hair occurs. Without a knowledge of this fact one would interpret the change in length as indicating a supersaturation of the air. For this reason we are of opinion that corresponding changes in hair-length in a balloon meteorograph cannot with any certainty be attributed to supersaturation. As the hygrometer in the balloon rises through a cloud it passes through a region of saturated air to air at lower relative humidity. It is likely, therefore, to show an initial expansion such as we obtained for the hair at a relative humidity of 100 per cent, when the relative humidity was decreased, for this preliminary change in length is immediate, while the change to the final length characteristic of the final relative humidity is slow.

If we compare our results with the recent experiments of Grundmann we would not expect him to have obtained the initial contraction on cooling a hair at a constant relative humidity, since he lowered his temperature much more slowly. He exhausted his chamber to a pressure of 1 mm. between the successive changes in relative humidity at a constant temperature, and this would account for his not observing the apparent supersaturation.

But the two sets of results differ in the sign of the expansion coefficient. Grundmann observes a positive coefficient over the range $+20°$ to $-50°$ C., whereas our coefficient changes from negative to positive as the temperature falls through $+1{\cdot}5°$ C. The main difference in the two sets of experiments appears to be in the load on a single hair, 0·5 g. in his case and 1·5 g. in ours.

§ 4. ACKNOWLEDGMENT

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THE VISCOSITIES OF SOME LIQUID REFRIGERANTS

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ABSTRACT. The viscosities of sulphur dioxide, ethyl chloride, methyl chloride, cis-dichlorethylene, trans-dichlorethylene, trichlorethylene and dichlor-difluormethane have been measured at temperatures between $-15°$ and $+30°$ C. The method used is that of timing the rate of fall of a closely fitting plug in a vertical tube filled with the liquid. In order to avoid evaporation, with the resultant formation of bubbles, an auxiliary reservoir of the fluid was connected with the experimental tube; the refrigerant in the reservoir was maintained at a temperature slightly above that of the tube, so that the pressure in the apparatus was above the vapour pressure of the liquid in which the plug moved. In all cases the viscosity η was found to follow a law $\eta = Ae^{a/T}$ where T is the absolute temperature and A and a are constants.

§ 1. INTRODUCTION

In the selection of a refrigerant, primary consideration has to be given to such physical properties as the boiling-point and specific volume; other properties, such as the viscosity and the thermal conductivity of the liquid, become of interest when the operation of the plant is being subjected to detailed analysis.

The viscosity of the refrigerant plays an important part in determining the rate of heat transfer in the evaporator and the condenser. In both these component parts, heat has to be transferred to or from a film of liquid to the metal pipe, and it is known that, in such problems of heat transfer, a determining variable is the Reynolds number Vd/ν where V is the velocity of the fluid, d the diameter of the pipe and ν the kinematic viscosity. The exact way in which the heat transfer depends on this and other variables is not yet fully elucidated and it is hoped to study this subject soon. It is clear that no progress will be possible in this direction unless data on the viscosity are available.

The compressor of a refrigerating plant has to act as a pump and to drive the fluid round the whole cycle, from compressor to condenser and thence through the throttle valve to the evaporator. In the central part of this path the refrigerant is in the form of liquid, and the resistance to flow, if the motion is stream-line, is directly proportional to the viscosity of the liquid.

§ 2. METHOD OF MEASUREMENT

The viscosities have to be measured at temperatures above the normal boiling-points of the fluids concerned, and hence the apparatus must be completely sealed so that the liquid can be maintained under pressure. It must also be of a form easy to surround with a cooling jacket, for work at low temperatures. Under these circumstances, the falling-plug method appears the most suitable.

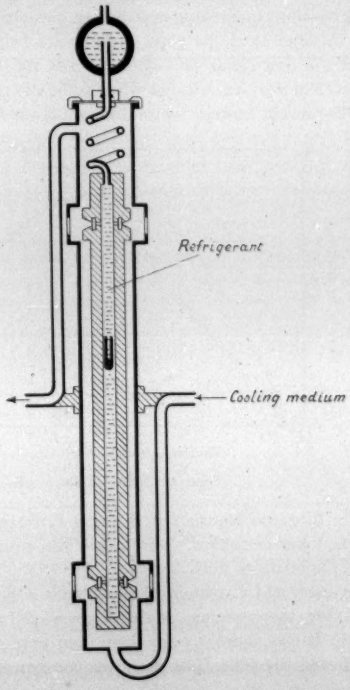

Figure 1. Viscosity apparatus (approximately quarter-scale).

The liquid was contained in a metal tube 8 mm. in diameter and 28 cm. long which had been machined so as to give it a very uniform bore. The tube was fitted with four windows in pairs diametrically opposite at each end. The windows had an aperture of about half a millimetre and a beam of light was directed through each pair. The time of transit of the plug along the central portion of the tube (22 cm.) was determined by noting the time of disappearance of the tail of the plug

at the upper windows and the appearance of the nose at the lower windows; this gave the time of passage of the plug along the uniform portion of the tube undisturbed by the presence of the holes for the windows.

In some of the experiments the windows were made of glass between lead washers. It was found that when distilled water was used as one of the liquids for calibrating the apparatus, the water attacked the lead, depositing a white film on the glass. Transparent bakelite windows held in position by invar washers were therefore used for the refrigerants other than sulphur dioxide. Liquid sulphur dioxide attacked the bakelite, so recourse was had to glass held between ebonite washers, the relative thicknesses of the glass and ebonite being so proportioned that the expansion of the unit (glass plus ebonite) was the same as that of brass. This avoided fracture of the glass window when sufficient pressure was applied between the washers to prevent leakage due to differential expansion.

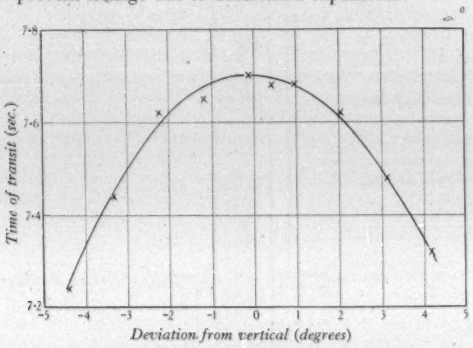

Figure 2. Effect of tilting tube.

The entire tube was sheathed in a jacket through which oil cooled by a refrigerating plant was circulated. This jacket was provided with windows in line with those in the viscosity tube.

The plug used had a cylindrical body with a hemispherical nose, and was hollowed out from the upper end so that it always fell vertically through the liquid (see figure 1). It was about 2·5 cm. long, and gave a clearance of about $\frac{1}{3}$ mm. between itself and the tube. The plug was constructed of the same brass as the tube.

Preliminary experiments with the tube filled with ether showed that the time of transit of the plug over the working section decreased appreciably when the axis of the tube deviated from the vertical. These results are shown in figure 2, where the time of transit of the plug is plotted against the deviation from the vertical in a definite plane. The actual position in which the tube was used was determined by finding the position at which the maximum time occurred, first in the plane to which figure 2 refers, and then in a plane perpendicular to this.

The apparatus was calibrated by observing the time of transit of the plug when the tube contained benzene, ether, pentane or water, each at a series of different temperatures. The viscosities of these materials were taken from the International Critical Tables, and they cover the sevenfold range from 0·24 to 1·68 centipoise. In figure 3, the results of the calibration are shown by plotting $T(\rho-\rho')$ against η, where T is the time of fall, ρ the density of the plug (8·6 g./cm.^{3}) and ρ' that of the liquid concerned, whilst η is its viscosity. It is worthy of note that the calibration points for benzene and water agree, although their densities differ by 12 per cent. Similarly, agreement is found between ether and pentane,

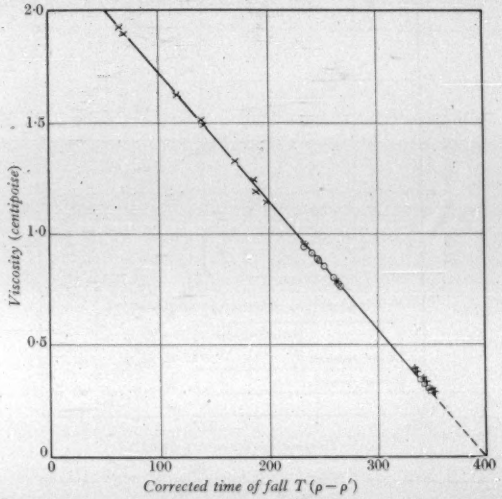

Figure 3. Calibration of apparatus. Water ×, benzene ⊙, ether +, pentane ⊡.

which differ by 11 per cent in density. This may be taken as evidence that the conditions under which the plug falls are such that the time of fall between the two windows depends only on the absolute, and not on the kinematic, viscosity. After the conclusion of the series, the calibration was repeated and found to have changed slightly. In preparing table 1 giving the smoothed results, the mean of the two calibration curves has been employed.

§ 3. RESULTS

In dealing with any one substance, three observations of the time of fall were taken at each temperature, using a stop watch divided to fifths of a second. In every case at least two samples of the liquid were used, to ensure that the results obtained in the first series had not been vitiated by accidental contamination with

impurities, or by the presence of a bubble of air or vapour. In each case, the results were also examined for a possible variation of viscosity with pressure over the small range of pressures used in the experiments concerned, but in no case could such a variation be detected with certainty.

As a typical example, figure 4 shows the results for sulphur dioxide. It will be seen that the observations taken at pressures above an arbitrary limit of 3·9 atmospheres agree with those taken below.

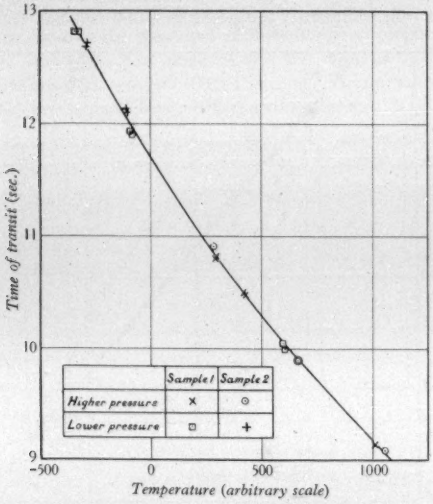

Figure 4. Sulphur dioxide.

The results for all the substances examined obey laws of the form $\eta = Ae^{a/T}$ where η is the viscosity and T the absolute temperature. Thus the experimental results lie on a straight line if the logarithm of the viscosity is plotted against the reciprocal of the absolute temperature. The observations plotted in this way for ethyl chloride, methyl chloride, cis-dichlorethylene, trans-dichlorethylene, trichlorethylene, dichlor-difluormethane (Freon) and sulphur dioxide are shown in figures 5 and 6, in which the reduction has been based on the initial calibration curve. Two samples of trans-dichlorethylene were studied, one of which contained about 10 per cent of the cis-compound, whilst the other was of higher purity. The viscosities only differed by about $\frac{1}{3}$ per cent. Values read from these curves and expressed as viscosities instead of logarithms are given in table 1, and it is of interest to notice that, despite the variety of compounds used, the viscosity of the most viscous is only about three times that of the most mobile.

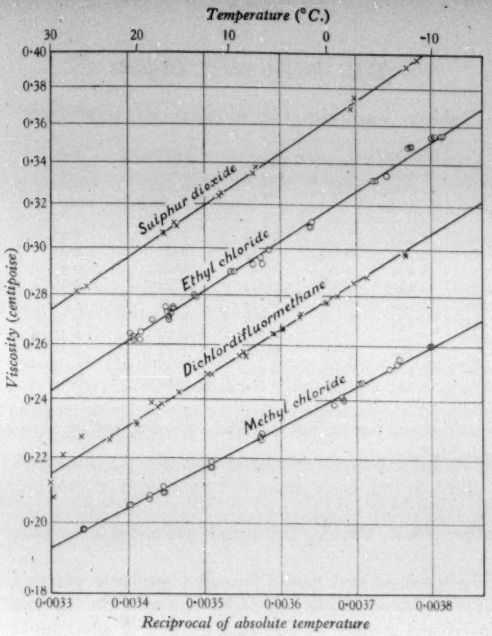

Figure 5.

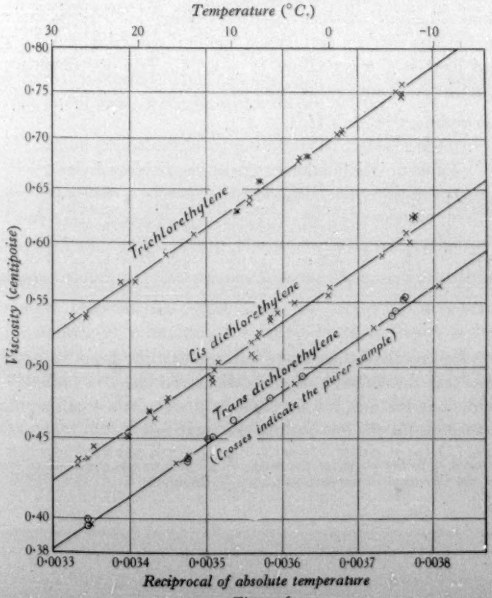

Figure 6.

Table 1. Viscosities of liquid refrigerants (centipoise)

Temperature	Methyl chloride CH_3Cl	Dichlor-difluor-methane $CCl_2.F_2$	Ethyl chloride C_2H_5Cl	Sulphur dioxide SO_2	Trans-dichlor-ethylene CHCl : CHCl	Cis-dichlor-ethylene CHCl : CHCl	Trichlor-ethylene $CHCl_3$
30	$0{\cdot}19_7$	$0{\cdot}21_9$	—	$0{\cdot}27_9$	0·39	0·43	0·53
25	$0{\cdot}20_3$	$0{\cdot}22_7$	$0{\cdot}25_9$	$0{\cdot}29_1$	0·41	0·45	0·56
20	$0{\cdot}21_0$	$0{\cdot}23_7$	$0{\cdot}26_9$	$0{\cdot}30_4$	$0{\cdot}42_5$	0·47	0·58
15	$0{\cdot}21_7$	$0{\cdot}24_7$	$0{\cdot}28_0$	$0{\cdot}31_8$	0·44	0·49	0·61
10	$0{\cdot}22_5$	$0{\cdot}25_8$	$0{\cdot}29_3$	$0{\cdot}33_4$	0·47	0·52	0·64
5	$0{\cdot}23_4$	$0{\cdot}27_0$	$0{\cdot}30_8$	$0{\cdot}35_0$	0·49	0·54	0·67
0	$0{\cdot}24_3$	$0{\cdot}28_3$	$0{\cdot}32_3$	$0{\cdot}36_8$	0·52	0·57	0·71
− 5	$0{\cdot}25_4$	$0{\cdot}29_8$	$0{\cdot}33_9$	$0{\cdot}38_9$	0·54	0·60	0·75
−10	$0{\cdot}26_5$	$0{\cdot}31_3$	$0{\cdot}35_8$	$0{\cdot}41_0$	0·57	0·64	0·79
−15	$0{\cdot}27_6$	$0{\cdot}32_2$	$0{\cdot}37_8$	$0{\cdot}43_4$	0·61	—	—

The compositions of the various materials, as obtained by chemical analysis, are also recorded below.

§ 4. CHEMICAL EXAMINATION OF SOME OF THE REFRIGERANTS*

Dichlor-difluormethane, CF_2Cl_2. This sample was tested for moisture and hydrochloric acid.

161 g. of the specimen were passed through phosphorus pentoxide tubes; the gain in weight of the latter was not measurable. 5 cm³ of the specimen with 5 cm³ of methyl alcohol and 4 drops of saturated solution of silver nitrate in methyl alcohol gave only a very slight turbidity.

The volume remaining undissolved after shaking 200 cm³ of the vapour with medicinal paraffin was only 3·2 cm³. When 100 cm³ were distilled the whole of the liquid distilled over at a temperature of −31° C. The specimen appears to be exceptionally pure for a commercial product.

Cis-dichlorethylene, CHCl : CHCl.

Table 2. Distillation range of cis-dichlorethylene

Temperature (°C.)	48–57	57–58	58–59·4	59·4–60·4	60·4–60·7	Residue
Fractions (per cent by weight)	6	10	11	67½	4	1½

The specific gravity at 15·5/15·5° C. was 1·2919. Acidity was very slight. No free chlorine was detected.

The figures for the distillation range indicate that the liquid is nearly pure cis-dichlorethylene and the content of trans-dichlorethylene is probably much less than 5 per cent since the first fraction (48–57°) contains a small amount of water which would account for the low boiling temperatures.

* The statements as to the purity of the materials given here are summarized from reports of analyses made at the Chemical Research Laboratory, Teddington.

Trans-dichlorethylene, CHCl : CHCl.

Table 3. Distillation range of trans-dichlorethylene

Temperature (°C.)	47–48	48–48·8	48·8–50·2	50·2–51·4	51·4–53·2	53·2–59·3	Residue
Fractions (per cent by weight)	5½	6	59	12	4	9½	4

The specific gravity at 15·5/15·5° C. was 1·2664. The acidity was very slight. No free chlorine was detected.

The figures for the distillation range indicate that the liquid probably contains over 10 per cent of the cis-dichlorethylene. (This sample is one of the two referred to in § 3. The purer sample consisted of the fraction of the original sample which boiled in the range 48·8–50·2° C.)

Methyl chloride, CH_3Cl. The methyl chloride supplied by the Imperial Chemical Industries was stated by them to be of a purity about 99·9 per cent.

Sulphur dioxide, SO_2. The gaseous phase contained 0·0025 per cent of weight of water and the liquid phase 0·025 per cent of water.

§ 5. DISCUSSION OF RESULTS

According to the theory of Kudar[1] the formula governing the variation of viscosity with temperature for an unassociated liquid should be $\eta = Ae^{Q/RT}$ where R is the gas-constant and Q the latent heat of fusion of the substance. Unfortunately these latent heats are unknown for the refrigerants tested, and therefore the truth of his theory cannot be tested. It is, however, of interest to calculate from figures 5 and 6 what the latent heats must be if the theory is true.

Table 4. Latent heats predicted by Kudar's theory

Substance	Dichlor-difluor-methane	Tri-chlor-ethylene	Trans-dichlor-ethylene	Cis-di-chlor-ethylene	Ethyl chloride	Sulphur dioxide	Methyl chloride
Latent heat of fusion (cal./g.)	11·73	11·82	16·35	16·53	22·71	23·87	24·31

A second method of estimating the latent heats of fusion is by an indirect comparison with the known latent heats of other substances. In Kaye and Laby's tables, the latent heats of eight compounds melting between −75° C. and +333° C. are given. From these data the mean value of ML/T, where M is the molecular weight, L the latent heat and T the melting point on the absolute scale is found to be 8·88 for the four with the lowest melting points (mean −14° C.) and 9·25 for the other four (mean 191° C.).

The melting point of dichlor-difluormethane is unknown, and the mean for the other six substances dealt with in the paper is $-88°$ C. If we assume therefore that ML/T for them would have a value about 8·75, obtained by extrapolation, then the latent heats can be estimated as shown in table 5.

Table 5

Substance	Tri-chlor-ethylene	Trans-dichlor-ethylene	Cis-di-chlor-ethylene	Ethyl chloride	Sulphur dioxide	Methyl chloride
Latent heat from viscosity	11·8	16·4	16·5	22·7	23·9	24·3
Latent heat by comparison with other substances	12·4	17·4	20·1	18·2	27·4	30·4

Close agreement cannot be expected, since the values assessed by comparison with other substances are likely to be in error by quite large amounts. Nevertheless, the order of magnitude is the same by the two methods, and thus the viscosity data appear to support the theory of Kudar, at least approximately. It is hoped to measure the latent heats of fusion of these materials in the near future, and thus to check the theory more accurately.

§ 6. ACKNOWLEDGMENTS

The work recorded in this paper was carried out at the request of the Engineering Committee of the Food Investigation Board, to whom we are indebted for permission to publish.

We are deeply indebted to Dr Guy Barr for his extremely helpful advice at various stages of the work, and we wish also to thank Mr A. Snow for his skilful assistance both in the constructional and the observational work.

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THE THERMAL AND ELECTRICAL CONDUCTIVITIES OF METALS AND ALLOYS: PART 2, SOME HEAT-RESISTANT ALLOYS FROM 0° C. TO 800° C.

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ABSTRACT. A comparative longitudinal-flow method has been used to determine the thermal conductivities, up to temperatures approaching 800° C., of F.N.C.T., F.H. stainless, Staybrite and Era A.T.V. steels, and of monel metal and an alloy composed of approximately 80 per cent of nickel and 20 per cent of chromium. The values are derived in terms of the thermal conductivity of a specimen of nickel-plated iron which had been previously tested over the full temperature-range. Determinations of the electrical resistivity are made in the course of the same experiment, and values of the Lorenz function are derived. Whereas at atmospheric temperature the values of the Lorenz function for these metals are abnormally high, and vary from $0{\cdot}76 \times 10^{-8}$ for the F.N.C.T. steel to $1{\cdot}18 \times 10^{-8}$ for the F.H. stainless steel, they decrease towards a common value with increase in temperature, and at 800° C. all lie between $0{\cdot}62 \times 10^{-8}$ and $0{\cdot}68 \times 10^{-8}$. An examination of values obtained for the Lorenz function of metals by other workers reveals that the extreme values so far published for this function over the temperature-range 400° to 1000° C. are $0{\cdot}56 \times 10^{-8}$ and $0{\cdot}80 \times 10^{-8}$. It is concluded that the thermal conductivity of a metal can be predicted with a fair degree of approximation over this range of temperature from a knowledge of the electrical resistivity, and that in general the probable error involved decreases as the temperature increases.

§ 1. INTRODUCTION

THIS paper forms part of a research which is directed towards an investigation, over a wide range of temperature, of the extent to which pure metals and various alloys obey the Wiedemann-Franz-Lorenz law.

At the time at which the work was commenced there was a scarcity of thermal-conductivity data for the stainless steels and nickel-chromium alloys, particularly at the high temperatures at which these heat-resistant alloys are frequently used in practice. Determinations made at moderate temperatures had indicated that in general these metals possessed a low thermal conductivity, and that the value of the Lorenz function might be expected to be abnormally high. It appeared, therefore, that measurements of the thermal and electrical conductivities of several commercial alloys of this type up to temperatures of the order of 800° C. might furnish results of considerable academic interest which should also be of practical value. During last year M. S. van Dusen and S. M. Shelton[1, 2] working at the Bureau of Standards have published values of the thermal conductivity of a number of

alloys of this class over a temperature-range of 100–550° C. The method which they employed was similar in principle to that which had been used for the present investigation, and it is satisfactory that in those cases in which materials of similar compositions have been tested the values are in good agreement.

§ 2. DESCRIPTION OF METALS TESTED

In each instance the specimens were obtained in the form of rods, approximately 3 in. in diameter and 15 in. long. Table 1 contains a description and analysis of the metals tested.

§ 3. METHOD OF EXPERIMENT

(i) *Range* 30–200° C. The rods were each machined to a uniform diameter of a little less than 3 in., and one end was fashioned so as to fit into the machined end of one of the Armco iron rods previously tested[3]. Holes for the insertion of thermocouples were drilled normal to the surface at distances of 6·0 and 25·4 cm. from this machined end. To this end was soldered a water-flow calorimeter, and the rod was then mounted vertically with the calorimeter uppermost, within a lagged guard tube about 6 in. in diameter. To prevent convection currents being set up the interspace was packed with silocel insulating powder. The rod was electrically heated at the base, and the guard tube adjusted to prevent lateral interchange of heat. The quantity of heat flowing in the rod was determined in terms of the rise in temperature of the water which flowed at a steady measured rate through the calorimeter. This temperature-rise was measured by means of differential thermocouples, and in order that it should remain constant in value the water was passed through a coil immersed in a thermostatically controlled bath immediately before entering the calorimeter. The latter and the tubes containing the thermocouple junction were well lagged to prevent any appreciable heat-interchange taking place. The temperature-gradient established in the specimen was measured by means of a single thermocouple which could be inserted into either of the two holes mentioned above.

This method was not used for mean temperatures above about 200° C. as this would necessitate the determination being made with very large temperature-gradients, but it was useful as a check on the results of the main experiment; moreover it enabled values of the thermal conductivity to be determined at temperatures as low as 30° C.

Each of the specimens was first tested in this manner over the range 30–200° C., and the results obtained were in good agreement with those of the main research.

(ii) *Range* 200–800° C. The method used for the measurement of thermal conductivity at higher temperatures is essentially a comparative one, in which the water-flow calorimeter is replaced by a rod of known conductivity, and the thermal conductivity of the alloy is deduced from measurements of the temperature-gradients established in the two rods when the same quantity of heat flows in each. One of the nickel-plated rods of Armco iron already tested was used as the metal of known conductivity.

Table 1. Particulars of metals investigated

Material	Supplied by	Description	Analysis												
			Fe	C	Ni	Cr	Mn	Si	Cu	W	S	P	Mg	Al	Co
F.N.C.T. steel	Brown Firth Research Laboratories	Oil hardened and tempered 830°/600° C.	94·36†	0·39	3·55	0·85	0·64	0·21	—	—	?	?	—	—	—
F.H. stainless steel		Air hardened 940° C. Tempered 725° C.	85·15†	0·27	0·37	13·65	0·29	0·27	—	—	?	?	—	—	—
Staybrite steel		Softened 1150°/1200° C.	73·49†	0·15	8·04	17·87	0·26	0·19	—	—	?	?	—	—	—
*Era A.T.V. steel	Hadfields, Ltd.	Forged steel	52·2†	0·46	26·86	15·20	1·18	1·30	—	2·77	0·014	0·018	—	—	—
*Monel metal	Monel-Weir, Ltd.	Hot rolled, black surface	1·72	0·16	67·10	—	0·98	0·01	29·18	—	0·014	0·024	0·13	0·04	0·33
*Coronil (70 Ni, 30 Cu)	H. Wiggin and Co., Ltd.	Forged and drawn	0·60	0·10	68·41	—	1·17	0·4	28·94	—	—	—	0·16	—	—
Nichrome (80 Ni, 20 Cr)	H. Wiggin and Co., Ltd.	Forged and drawn	0·59	0·12	77·28†	20·98	0·65	0·38	—	—	—	—	—	—	—

* The author is indebted to Mr T. E. Rooney of the Metallurgy Department, National Physical Laboratory, for these analyses, and to the manufacturers for the other analyses and descriptions.

† These figures have been derived by difference.

In order to join the test specimen to the iron a tin bath was first used. This proved satisfactory during assembly and at the lower temperatures, but after pro-

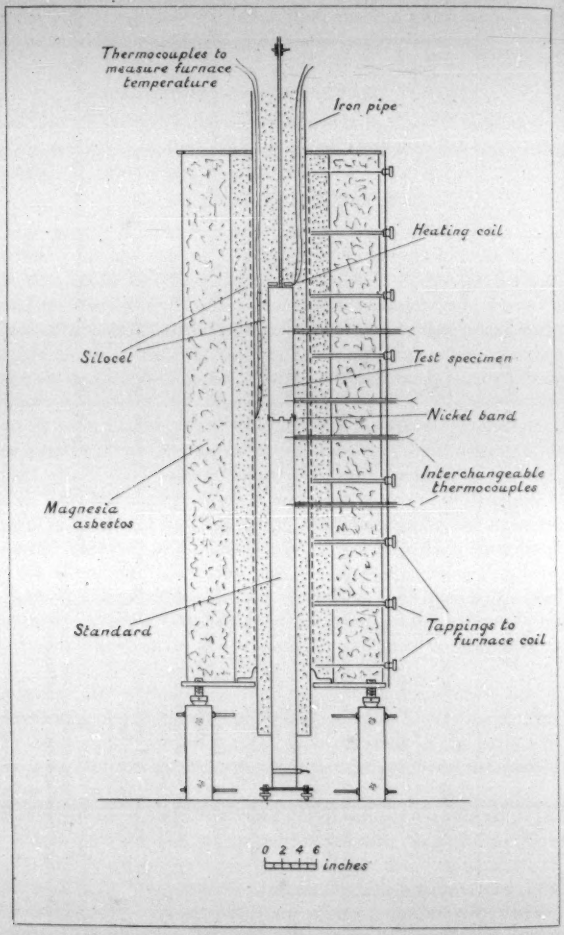

Figure 1. Apparatus for measuring thermal conductivity.

longed heating at high temperatures the tin underwent oxidation, and the thermal contact between the rods became unsatisfactory. It was afterwards found that good

thermal contact could be maintained if, in addition to the tin bath, a strip of nickel about 0·2 cm. thick and 1·5 cm. wide was screwed into position so as to form a band covering the junction of the rods. When the rods were being joined together care was taken to ensure that they should be in line with one another, and that all four thermocouple holes should be in one plane. Three thermocouples composed of fine platinum and platinum-rhodium wires were pegged into small holes drilled in each rod, and a steel rod $\frac{1}{4}$ in. in diameter and 2 ft. in length was screwed into the centre of the upper end of the test bar.

The composite rod, with the test specimen uppermost, was then lowered into position in the furnace which had been used for the earlier measurements on the

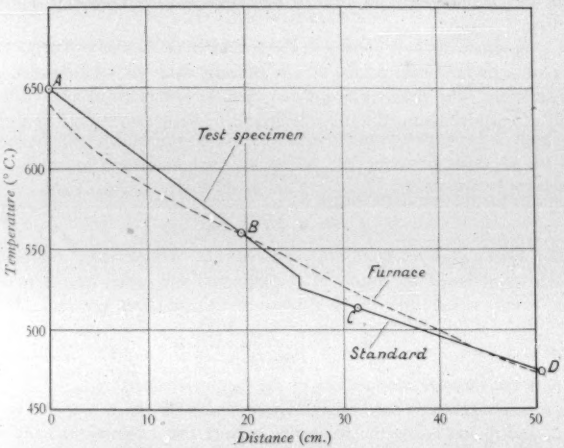

Figure 2. Example of temperature-distributions of central rods and furnace.

iron rods. The thermocouple holes were aligned with those in the furnace wall and the silica sheaths were inserted. A nichrome heating-coil wound in a flat spiral and embedded in a disc of steatite was dropped over the projecting steel rod on to the upper end of the specimen, and the furnace was packed with silocel powder. The steel rod served as one electrode when the resistance of the alloy was being measured, the other electrode being pegged into the lower end of the iron rod. The assembled apparatus is shown in figure 1.

The actual experimental method was very similar to that already described in the case of iron, except that in this instance no measurements were made of the electrical energy supplied to the specimen. Instead, this was derived in terms of the thermal conductivity of the standardized rod, and the measured temperature gradient therein, when lateral interchange of heat was prevented by carefully matching corresponding points of the rod and surrounding tube. Owing to the

sudden change in gradient which occurred at the junction of the two metals an exact match was not always possible, and in these cases a small correction has to be applied before the true thermal conductivity of the alloy can be obtained. A typical example of the temperature-distributions of the furnace and centre rods is shown in figure 2, and this may be used to illustrate the manner in which the correction is derived. The points marked A, B, C and D denote the positions and temperatures of the rod recorded by the interchangeable thermocouple; C and D are in the standard, and A and B in the test material, Era A.T.V. It will be observed that there is a drop of about 7° C. at the junction of the two rods, but the effect of this does not appear to be serious provided that the adjacent furnace is not too different in temperature. The mean temperature of the furnace is given by the dotted line.

x, a, b, c Let x represent the heat flowing in the specimen at A, and a, b and c (with the appropriate signs) the heat gained or lost laterally over the sections AB, BC and CD respectively. The gradient dT_T/dl_T in the test specimen of area A_T and conductivity K_T can be assumed to be established by the mean energy flowing in the section AB,

T_T, l_T, A_T
K_T

i.e. $$K_T A_T dT_T/dl_T = x + a/2,$$

and similarly for the standard (suffix S)

$K_S, A_S,$
T_S, l_S
h $$K_S A_S dT_S/dl_S = x + a + b + c/2,$$

giving $K_T A_T dT_T/dl_T = K_S A_S dT_S/dl_S - a/2 - b - c/2$. Approximate values for a, b and c can be obtained by means of the equation for radial heat-flow h which, however, is only strictly true in the absence of a longitudinal gradient. Thus

$$h = \frac{2{\cdot}73K\,(T_S - T_F)\,L}{\log_{10} r_F/r_S},$$

K, T_F where K is the thermal conductivity of the lagging-material, $(T_S - T_F)$ the mean difference in temperature between the specimen and furnace over the section of

L, r_S, r_F length L, and r_S and r_F are the respective radii of the specimen and the furnace. Assuming the thermal conductivity of silocel to be 0·0002 c.g.s. unit the values of a', b' and c' become respectively 0·035, 0·022 and 0·035 calories per degree of mean difference in temperature between the specimen and furnace. The actual mean differences in temperature for the three sections are 10·7°, 8·1° and 2·7° C. From which it is seen that $a = -0{\cdot}378$, $b = 0{\cdot}178$, and $c = 0{\cdot}095$ calories.

For this particular experiment the temperatures at A, B, C and D are 648·2, 559·8, 512·9 and 473·1 respectively; $L_T = L_S = 19{\cdot}4$ cm., $A_T = 42{\cdot}32$ cm.^{2}, $A_S = 42{\cdot}45$cm.^{2}, and at 493° C. $K_S = 0{\cdot}1056$ c.g.s. unit. Hence $K_T = 0{\cdot}0479$ c.g.s. unit. This is the thermal conductivity of the test specimen at a mean temperature of 604° C. In this experiment the correction for the lateral heat-transfer amounted to 0·4 per cent of the heat flowing in the standard rod.

At each mean temperature the relative temperatures of the furnace and specimen were adjusted so that the above correction assumed both positive and negative values, and the mean conductivity was determined from about six experiments of this kind.

The electrical conductivity was measured at the same time by passing a current of the order of 60 amperes through the rod, and comparing the potential-drop down a section of the rod with that across a standardized resistance connected in series with it. The thermocouples attached to the rod were used as the potential leads, the direction of the current being reversed in order to enable thermal e.m.fs. to be eliminated. In this manner determinations of the thermal and electrical conductivity of each alloy were made at a series of increasing mean steady temperatures up to nearly 800° C. A few repeat points were obtained during cooling, and in no instance did the difference due to heat treatment exceed 4 per cent.

§ 4. TABULATED RESULTS AND COMPARISON WITH OTHER WORKERS

In the tables which follow the values of the thermal conductivity K, in c.g.s. units, the electrical resistivity ρ in ohm-cm. and the Lorenz function, $K\rho/T$, where T is the absolute temperature, have been interpolated from the experimental results for every 100° C. from 0° to 800° C. A certain amount of extrapolation has been necessary in deriving the values at the two extreme temperatures of 0° and 800° C., and the values are bracketed for this reason. Reference is made to the results obtained by other workers where these are available for materials of similar compositions.

K
ρ

(*a*) *F.N.C.T. steel*

Property \ Temp. (° C.)	0	100	200	300	400	500	600	700	800
K	(0·080)	0·086	0·089	0·090	0·088	0·084	0·075	0·067	(0·059)
$10^6 \times \rho$	(26·0)	31·7	38·4	46·3	55·7	67·0	80·3	98·4	(124)
$10^8 \times K\rho/T$	(0·76)	0·73	0·72	0·72	0·73	$0·72_5$	0·69	$0·67_5$	(0·68)

(*b*) *F.H. stainless steel*

Property \ Temp. (° C.)	0	100	200	300	400	500	600	700	800
K	$(0·058_5)$	0·060	0·061	$0·061_2$	$0·061_3$	$0·061_4$	$0·061_3$	0·059	$(0·056_5)$
$10^6 \times \rho$	(55·0)	63·4	71·8	80·2	88·5	97·0	105·6	114·1	(122·7)
$10^8 \times K\rho/T$	$(1·17_7)$	1·02	$0·92_6$	$0·85_7$	$0·80_6$	$0·77_2$	$0·74_1$	$0·69_2$	$(0·64_8)$

S. M. Shelton[2] measured the thermal conductivity of two chromium steels somewhat similar to the above, the analyses and values being:

Chemical composition							Thermal conductivity at various temperatures (° C.)				
C	Mn	P	S	Si	Ni	Cr	100	200	300	400	500
0·07	0·09	0·015	0·010	0·09	0·23	12·00	0·0595	0·0619	0·064	0·0662	—
0·14	0·19	0·020	0·015	0·12	0·70	14·60	0·0581	0·0590	0·0602	0·0612	0·0625

These values are seen to be in reasonably good agreement with those obtained in the present investigation.

(*c*) *Staybrite steel*

Property \ Temp. (° C.)	0	100	200	300	400	500	600	700	800
K	(0·035$_8$)	0·039	0·042	0·045	0·049	0·052	0·056	0·059	(0·062$_5$)
$10^8 \times \rho$	(66·3)	74·3	81·9	89·1	95·0	100·1	104·8	109·4	(114·0)
$10^8 \times K\rho/T$	(0·86$_5$)	0·77$_4$	0·72$_7$	0·70$_4$	0·69	0·67$_3$	0·67	0·66$_4$	(0·66$_4$)

S. M. Shelton[2] has also examined three "18/8" stainless steels having similar compositions to this alloy, and obtained values in agreement with the present determination. Data for his specimens are set out below.

Chemical composition				Thermal conductivity at various temperatures (° C.)				
C	Mn	Ni	Cr	100	200	300	400	500
0·07	0·27	9·10	18·6	0·0392	0·0423	0·0454	0·0485	0·0516
0·11	0·19	9·21	18·5	0·0390	0·0421	0·0452	0·0480	0·0511
0·24	0·37	8·96	19·6	0·0373	0·0411	0·0447	0·0483	0·0519

The value of 0·033 is given for the thermal conductivity of Staybrite steel in *The development of Staybrite steel—Its properties and uses*, published by Thos. Firth and Sons, Ltd. The specific resistance in the fully softened condition is stated to be 69×10^{-6}. These values are presumably at atmospheric temperature. The increase in resistance with rise in temperature of Staybrite in the heat treated condition is shown over the range 18–300° C. by means of a curve, with which the present results are in general agreement.

(*d*) *Era A.T.V.*

Property \ Temp. (° C.)	0	100	200	300	400	500	600	700	800
K	(0·026)	0·030	0·033	0·037	0·040	0·044	0·047	0·051	(0·054)
$10^6 \times \rho$	(98·0)	102·7	106·9	111·0	114·2	117·3	120·1	122·2	(123·6)
$10^8 K\rho/T$	(0·95)	0·82	0·75	0·71	0·68	0·66$_5$	0·65	0·63$_5$	(0·62)

(*e*) 80 *per cent nickel and* 20 *per cent chromium*

Property \ Temp. (° C.)	0	100	200	300	400	500	600	700	800
K	(0·030)	0·033$_5$	0·037$_5$	0·041$_8$	0·045	0·051	0·055	0·059	(0·063)
$10^6 \times \rho$	(107·3)	108·3	109·0	110·0	110·8	111·3	111·4	110·3	(110·2)
$10^8 \times K\rho/T$	1·14	0·98	0·86$_5$	0·79$_5$	0·74$_8$	0·73	0·70	0·67	(0·64$_8$)

Ellis, Morgan and Sager[4] obtained values of 0·0358, $109·7 \times 10^{-6}$ and $1·29 \times 10^{-8}$ for the thermal conductivity, specific resistance and Lorenz function of an 80 per cent nickel and 20 per cent chromium alloy at a temperature of 32° C., whilst the

corresponding values obtained by Kikuchi[5] at 36° C. are $0{\cdot}031_2$, 105×10^{-6} and $1{\cdot}06 \times 10^{-8}$. The present values are in general agreement with the average results from these two determinations, and with the values of the thermal conductivity obtained by van Dusen and Shelton[1] which are 0·325 at 100° C., 0·0368 at 200° C., 0·0411 at 300° C., 0·0452 at 400° C., and 0·0492 at 500° C. Mention might be made of the fact that the experimental results of this alloy show a discontinuity in the thermal-conductivity-temperature curve at a little below 500° C. The specific

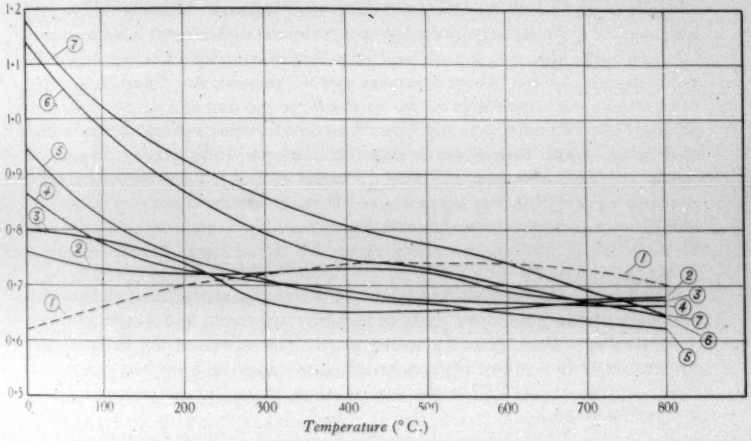

Figure 3. Variation of Lorenz function with temperature. (1) Armco iron; (2) F.N.C.T. steel; (3) Monel metal; (4) Staybrite steel; (5) Era A.T.V. steel; (6) Nichrome (80% Ni, 20% Cr); (7) F.H. stainless steel.

resistance has a maximum value at about 600° C. and the values obtained during both heating and cooling are in agreement beyond this temperature. As the metal was cooled below 530° C. the values of the resistivity increased about 2 per cent above those obtained at the corresponding temperature during heating and remained at about this level during the subsequent cooling to room temperature. It would appear that this alloy undergoes some definite change in the neighbourhood of 500° C.

(*f*) *Monel metal*

Property \ Temp. (° C.)	0	100	200	300	400	500	600	700	800
K	(0·051)	0·058	0·066	0·073	0·080	0·088	0·095	$0{\cdot}102_5$	(0·110)
$10^6 \times \rho$	(42·9)	50·1	53·2	52·5	54·6	57·7	60·8	63·3	(65·7)
$10^8 \times K\rho/T$	(0·80)	0·78	0·74	0·67	0·65	$0{\cdot}65_5$	0·66	0·67	$(0{\cdot}67_5)$

These values for the thermal conductivity are in reasonable agreement with those published by the Mond Nickel Company Ltd.[6] for metals of composition 70 per cent nickel and 30 per cent copper in the annealed condition. It is stated that a method similar to that used by Schofield[7] was employed, the following values being obtained, 0·062, 0·065, 0·076 and 0·078 c.g.s. unit at temperatures 94, 288, 421 and 439° C. respectively. The value of the specific resistance at atmospheric temperature is given as 42×10^{-6} ohm-cm.

Somewhat higher values have been obtained for the thermal conductivity of alloys of approximately this composition by other workers. Donaldson[8] tested a specimen of the following percentage composition, nickel 67·05, copper 29·07, iron 2·68, manganese 0·84 and silicon 0·30 and obtained values of 0·07, 0·077, 0·080 and 0·084 c.g.s. unit at 100, 200, 300 and 400° C. respectively. Smith[9] records a value of 0·069 c.g.s. unit at 57° C. for an alloy of 70 per cent nickel and 30 per cent copper, whilst Ellis, Morgan and Sager[4] included in the investigation, to which mention has already been made, an alloy containing 70 per cent nickel, 28 per cent copper and 2 per cent iron, and obtained values of 0·0832 c.g.s. unit, $42{\cdot}6 \times 10^{-6}$ ohm-cm. and $1{\cdot}16 \times 10^{-8}$ at a temperature of 32° C. for the thermal conductivity, specific resistance and Lorenz function respectively.

(*g*) *70 per cent nickel and 30 per cent copper*

Tests on the alloy described in table 1 as having this approximate composition were only carried out in the lower-temperature apparatus, the results obtained being similar to those given by monel metal. The values of the thermal conductivity could be represented by a straight line extending from 0·051 c.g.s. unit at 0° C. to 0·069 at 200° C. The electrical resistivity at atmospheric temperature was 46×10^{-6} ohm-cm.

§ 5. DISCUSSION OF THE RESULTS FOR THE LORENZ FUNCTION

The results obtained for the Lorenz function of the alloys tested are plotted in figure 3. It will be seen that in the neighbourhood of atmospheric temperature there are considerable departures from the normally accepted value of about $0{\cdot}55 \times 10^{-8}$. The present values invariably exceed this figure, those for the nickel-chromium alloy and F.H. stainless steel being more than twice as great. Had the Wiedemann-Franz-Lorenz law been assumed to hold good for these alloys, and an attempt made to derive the value of the thermal conductivity from a knowledge of the electrical resistance, the value obtained would have been less than half of the true value.

With increase in temperature the values of the Lorenz function are seen to alter considerably and to tend towards mean values of about $0{\cdot}7 \times 10^{-8}$ at 600° C. and $0{\cdot}65 \times 10^{-8}$ at 800° C. From this result it is apparent that the thermal conductivity of alloys of the type considered can be deduced indirectly from electrical-resistance measurements with considerably greater certainty at higher temperatures. By assuming the aforementioned mean values for the Lorenz function the thermal

conductivity could presumably be predicted to within 10 per cent over the temperature-range 600–800° C. At present there is a scarcity of experimental data for metallic conductors at high temperatures and this conclusion may prove to be somewhat limited in its range of applications. A certain amount of support for a convergence of values of the Lorenz function as the temperature is increased is, however, given by the results of Lees[10] and other workers at low temperatures. The values of the Lorenz function for the metals bismuth and antimony, and the alloys German silver, manganin, platinoid and lipowitz metal are all abnormally high at a temperature of −170° C., ranging from $1{\cdot}56 \times 10^{-8}$ to $0{\cdot}90 \times 10^{-8}$ for the last-mentioned four, but decrease as the temperature is increased, so that at 18° C. the values lie within the limits $0{\cdot}81 \times 10^{-8}$ and $0{\cdot}72 \times 10^{-8}$. On the other hand highly conducting metals, such as copper and aluminium, possess abnormally low values of the Lorenz function at extremely low temperatures, which increase to values mostly lying between $0{\cdot}5 \times 10^{-8}$ and $0{\cdot}6 \times 10^{-8}$ at atmospheric temperature, and frequently continue to increase slowly with further increase in temperature.

With regard to determinations at high temperatures, Schofield[7] has shown that the value for copper increases only from $0{\cdot}55 \times 10^{-8}$ to $0{\cdot}57 \times 10^{-8}$, and then decreases slightly again over the range from 100° to 600° C., whereas for aluminium it increases from $0{\cdot}53 \times 10^{-8}$ at 100° C. to $0{\cdot}60 \times 10^{-8}$ at 400° C. For nickel the value increases up to the temperature of the magnetic transformation point and thereafter remains fairly constant to 700° C., having a value of about $0{\cdot}64 \times 10^{-8}$.

Holm and Störmer[11] have measured the thermal and electrical conductivities of platinum over the range 19–1020° C., and have found the Lorenz function to increase from $0{\cdot}61 \times 10^{-8}$ to a maximum of $0{\cdot}71_5 \times 10^{-8}$ at about 800° C. and then decrease to $0{\cdot}68_5 \times 10^{-8}$ at 1020° C.

Honda and Simidu[12] tested nickel, Swedish iron, and a number of carbon steels up to about 900° C., and an examination of their data shows that over the temperature-interval 600–900° C. all values for the Lorenz function lie between $0{\cdot}64 \times 10^{-8}$ and $0{\cdot}80 \times 10^{-8}$.

The only other experiments within this temperature-range which have come to the notice of the present author are those of Angell[13] and Sager[14]. The former shows the Lorenz function of aluminium to increase from $0{\cdot}54 \times 10^{-8}$ to $1{\cdot}21 \times 10^{-8}$ over the range 100–600° C. and that of nickel to decrease from $0{\cdot}74 \times 10^{-8}$ at 300° C. to $0{\cdot}34 \times 10^{-8}$ at 700° C., whilst the latter gives a value as high as $1{\cdot}10 \times 10^{-8}$ for nickel at 700° C. Angell used the radial-flow method, and probably endeavoured to deal with too small a difference in temperature, whilst Sager, who also tested a number of nickel-copper alloys, adopted King's[15] suggested periodic-flow method for measurements at high temperature. The term used in the equation to represent the heat-loss from the surface due to radiation is a function of the difference in temperature between the wire under test and the enclosure, instead of the difference between the fourth powers of these temperatures, which may account for the high values obtained for the thermal conductivity at high temperatures.

When the results of these last two experiments are omitted it is found that the values of the Lorenz function of all metals so far tested over the range 400–1000° C. lie between $0{\cdot}56 \times 10^{-8}$ and $0{\cdot}80 \times 10^{-8}$.

§ 6. ACKNOWLEDGMENTS

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THE MECHANICAL FORCE ON BODIES OF SMALL SUSCEPTIBILITY DUE TO INDUCED MAGNETIZATION

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ABSTRACT. The mechanical force on a body of any shape and of small susceptibility, when placed in a magnetic field, is expressed as an integral taken over the surface of the body. This principle is applied to the experimental arrangement adopted in Rankine's magnetic torsion balance, where a magnetic pole is attracted by the magnetization induced in a spherical body. The results obtained are (1) a direct proof of Rankine's formula for a point pole; (2) the correction for the earth's field; and (3) the correction for the finite spread of the poles in an actual magnet.

§ 1. INTRODUCTION

Rankine's recent adaptation[1] of the magnetic torsion balance to the measurement of the paramagnetism of substances of small susceptibility has drawn attention anew to the classical problem of the calculation of the mechanical forces on a body due to its induced magnetization. In the general case we have to consider a body of specified form with uniform susceptibility κ, and an applied field of variable magnetic intensity $\mathbf{H}$. When no restriction is placed on the value of κ, the problem is effectively soluble only for bodies with certain specified forms, e.g. a cylinder, a sphere or an infinite plane. The only obvious general result is that the resultant mechanical force and couple due to the action of the applied field on the induced magnetization will always be zero if the applied field is uniform in magnitude and direction. In other words, the resultant force and couple are due to the non-uniformity of the applied field in the neighbourhood of the body.

In the special cases considered by Rankine, however, the susceptibility is always small, typical values being $3{\cdot}2 \times 10^{-8}$ for air and -7×10^{-7} for water. In these circumstances a simple and general solution, valid to a high degree of approximation, can be found in the form of an integral taken over the surface of the magnetizable body. Rankine himself has considered the particular problem of the attraction of a paramagnetic sphere by a magnetic pole and has deduced a simple, approximate expression for the force, valid for small κ, from the complex, exact expression given by Jeans for any value of κ. It is a matter of interest to obtain this particular approximate result directly and it may be easily found from the general approximate result in the form of a surface integral.

§ 2. THE INDUCED MAGNETIZATION

The general approximate result is that the induced magnetization is equivalent to a layer of magnetic matter distributed over the surface of the magnetizable body with surface density σ equal to $\kappa H_0^{(n)}$ when $H_0^{(n)}$ is the component of the magnetic intensity of the applied field along the outward-drawn normal to the surface of the body. The error involved in this approximate result is of the order of magnitude of κ^2, and is therefore usually negligible. This result can be established either (*a*) by the use of the conditions of continuity at the boundary of the magnetic media or (*b*) by the use of Poisson's transformation.

σ, $H_0^{(n)}$

$\mathbf{H}_0$, V_0, V, U

S

(*a*) Let the magnetic potential of the applied field $\mathbf{H}_0$ be V_0 and let V, U be the potentials due to the induced magnetization at points which are respectively outside and inside the magnetizable body. Then the boundary conditions at the surface S of the body are

$$V_0+V=V_0+U,$$

$$\frac{\partial V_0}{\partial n}+\frac{\partial V}{\partial n}=(1+4\pi\kappa)\left\{\frac{\partial V_0}{\partial n}+\frac{\partial U}{\partial n}\right\},$$

n

where the differentiations are along n, the outward-drawn normal to S. Now V and U are expressible in the forms,

$$V=\kappa V_1+\kappa^2 V_2+\ \ldots\ +\kappa^n V_n+\ \ldots,$$

$$U=\kappa U_1+\kappa^2 U_2+\ \ldots\ +\kappa^n U_n+\ \ldots,$$

V_n, U_n

where V_n, U_n are potential functions independent of κ. Hence at points on S, V_1 and U_1 must satisfy the boundary conditions,

$$V_1=U_1,$$

$$\frac{\partial V_1}{\partial n}-\frac{\partial U_1}{\partial n}=4\pi\frac{\partial V_0}{\partial n}.$$

It follows that V_1 and U_1 are the values of the potential, outside and inside S respectively, due to a surface layer of density $-\partial V_0/\partial n=H_0^{(n)}$, the component of the applied field $\mathbf{H}_0$ along the outward-drawn normal to S. Now to the first order of approximation κV_1 and κU_1 are the values of the potential due to the induced magnetization. Hence the induced magnetization is equivalent to a surface layer of density $\kappa H_0^{(n)}$.

$\mathbf{I}$

R

(*b*) Let $\mathbf{I}$ be the intensity of the induced magnetization at a point Q in the body, and let R be the distance from Q to an external field point P. Then the corresponding potential V is given by

$$V=\int \mathbf{I}.\operatorname{grad}\frac{1}{R}\,dv,$$

the differentiation implied in the operator "grad" being with respect to the coordinates of Q and the integral being taken throughout the volume occupied by the body. Now

$$\mathbf{I}.\operatorname{grad}\frac{1}{R}=\operatorname{div}\left\{\frac{\mathbf{I}}{R}\right\}-\frac{1}{R}\operatorname{div}\mathbf{I}$$

and

$$\operatorname{div}\mathbf{I}=\operatorname{div}(\kappa\mathbf{H})=0,$$

$\mathbf{H}$ being the total intensity of the magnetic field at Q. Hence

$$V = \int \operatorname{div} \left\{\frac{\mathbf{I}}{R}\right\} dv = \int \frac{1}{R} I^{(n)}\, dS$$

$$= \int \frac{\kappa}{R} H^{(n)}\, dS,$$

the (n) denoting the normal component and the integrals now being taken over the surface of the body.

The corresponding magnetic intensity due to the induced magnetization is

$$\mathbf{H} - \mathbf{H}_0 = \kappa \int \frac{H^{(n)}}{R^3}\, \mathbf{R}\, dS,$$

where $\mathbf{R}$ is the vector drawn from Q on S to the field point P. The accurate expression for the equivalent surface density σ of the induced magnetization is therefore given by

$$\sigma = \kappa H^{(n)} = \kappa H_0^{(n)} + \kappa^2 \int \frac{H^{(n)} R^{(n)}}{R^3}\, dS \qquad \ldots\ldots(2{\cdot}1),$$

by the preceding equation. The second term here gives the error in the approximate formula $\sigma \fallingdotseq \kappa H_0^{(n)}$. It is equal to the normal intensity due to a surface layer of density $\kappa^2 H^{(n)}$ and hence its order of magnitude is $2\pi\kappa^2 H^{(n)}$ or $2\pi\kappa^2 H_0^{(n)}$.

§ 3. THE MECHANICAL FORCES

Since the induced magnetization is equivalent to a surface layer of density $\sigma \fallingdotseq \kappa H_0^{(n)}$, the mechanical forces on the magnetizable body are clearly equivalent to a surface distribution of force of an intensity per unit area equal to

$$\sigma \mathbf{H}_0 \fallingdotseq \kappa H_0^{(n)} \mathbf{H}_0 \qquad \ldots\ldots(3{\cdot}1).$$

In most practical cases part of the applied field $\mathbf{H}_0$ will consist of the magnetic field of the earth, say $\mathbf{E}_0$, and it is easily seen that, although the earth's field is sensibly uniform throughout the dimensions of laboratory apparatus, its effect is by no means negligible. For if

$$\mathbf{H}_0 = \mathbf{E}_0 + \mathbf{F}_0,$$

the resultant force on the body is

$$\kappa \int H_0^{(n)}\, \mathbf{H}_0\, dS = \kappa \mathbf{E}_0 \int H_0^{(n)}\, dS + \kappa \int H_0^{(n)}\, \mathbf{F}_0\, dS.$$

But

$$\int H_0^{(n)}\, dS = 0.$$

Hence the force is

$$\kappa \int F_0^{(n)}\, \mathbf{F}_0\, dS + \kappa \int E_0^{(n)} \mathbf{F}_0\, dS \qquad \ldots\ldots(3{\cdot}2),$$

i.e. it is simply the sum of the forces exerted by the field $\mathbf{F}_0$ on the induced magnetization due to the earth's field $\mathbf{E}_0$ and on the induced magnetization due to the field $\mathbf{F}_0$.

In Rankine's method it is more convenient to measure the mechanical force exerted on the magnet producing the field, rather than the force exerted on the magnetizable body, but here again it is necessary to allow for the effect of the earth's

field. Clearly the force exerted on the magnet by the body is equal and opposite to the force exerted on the body by the magnet, and this latter is

$$\int \sigma \mathbf{F}_0 \, dS = \kappa \int H_0^{(n)} \mathbf{F}_0 \, dS$$
$$= \kappa \int F_0^{(n)} \mathbf{F}_0 \, dS + \kappa \int E_0^{(n)} \mathbf{F}_0 \, dS,$$

i.e. the same result as before is obtained. Although the second term, due to the earth's field, is in general not zero, it can be made to vanish in the experimental arrangement adopted by Rankine, as is shown below.

m The simplest general case arises where the applied field is due to a magnetic pole of strength m placed very near to the body. In these circumstances the surface of the body can be regarded as an infinite plane. If the shortest distance of the p, r, θ pole from the body is p, the distance r in a direction making an angle θ with the shortest distance is $p \sec \theta$. The equivalent surface density σ at the point (r, θ) is given by

$$\sigma = \kappa (m/r^2) \cos \theta + \kappa E_0^{(n)},$$

allowing for the component of the earth's field normal to the surface. Hence the resultant attraction on the body or on the pole is

$$\int \sigma (m/r^2) \cos \theta \, dS,$$

where

$$dS = d [\pi (p \tan \theta)^2]$$
$$= 2\pi p^2 \tan \theta \sec^2 \theta \, d\theta.$$

Hence the resultant attraction is

$$(\pi \kappa m^2/2p^2) + 2\pi \kappa m E_0^{(n)} \qquad \ldots\ldots(3{\cdot}3).$$

The presence of the second term involving $E_0^{(n)}$ illustrates the general conclusion reached in the last paragraph.

c, a In the case considered by Rankine the magnetic pole S is at a horizontal distance c from the centre of a magnetizable sphere of centre C and radius a. The other pole N of the magnet is vertically below S and exerts a negligible effect. Neglecting at first the effect of the earth's field, the attractive force on the magnetic pole can be calculated as follows:

R_1, R_2 If a straight line SP_1P_2 is drawn through S making an angle θ with SC, it will meet the surface of the sphere at points P_1 and P_2 at distances R_1 and R_2 from S where

$$R_1 R_2 = c^2 - a^2$$

and

$$\tfrac{1}{2} (R_1 + R_2) = c \cos \theta.$$

ψ At P_1 and P_2, $H_0 = m/R_1^2$ and m/R_2^2 and the values of the surface density σ are $-\kappa m \cos \psi / R^2$ and $+\kappa m \cos \psi / R^2$ respectively, ψ being the angle between the normals to the sphere at P_1, P_2 and the line SP_1P_2. Hence the induced pole-dS_1, dS_2 strengths on surface elements dS_1 and dS_2 at P_1 and P_2 are respectively

$$-\kappa m \cos \psi \, dS_1/R_1^2 \quad \text{and} \quad +\kappa m \cos \psi \, dS_2/R_2^2;$$

$d\omega_1, d\omega_2$ i.e. $\kappa m d\omega_1$ and $\kappa m d\omega_2$, where $d\omega_1$ and $d\omega_2$ are the solid angles subtended at S by dS_1 and dS_2. The mechanical forces on these elements of area parallel to SC are therefore

$$\kappa m^2 \cos \theta \, d\omega_1 / R_1^2 \quad \text{and} \quad \kappa m^2 \cos \theta \, d\omega_2 / R_2^2.$$

Now, if we take spherical polar co-ordinates (θ, ϕ) with pole at S and SC as axis,

$$d\omega_1 = -\sin\theta\, d\theta d\phi \quad \text{and} \quad d\omega_2 = +\sin\theta\, d\theta d\phi.$$

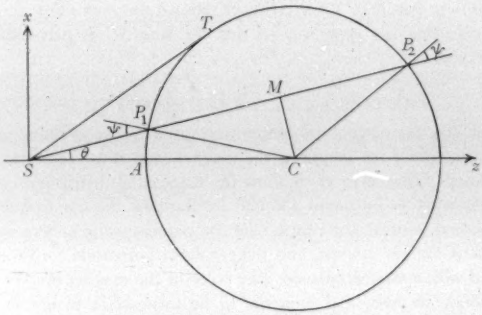
Hence the total attraction on the sphere parallel to CS is

$$F = \kappa m^2 \int_0^\alpha \left\{\frac{1}{R_1^2} - \frac{1}{R_2^2}\right\} \cos\theta \sin\theta\, d\theta \int_0^{2\pi} d\phi,$$

where α is the value of θ for the tangent ST from S to the sphere, i.e. α

$$\sin\alpha = a/c = s, \text{ say.} \qquad s$$

Now
$$R_2^2 - R_1^2 = (R_2 + R_1)(R_2 - R_1)$$
$$= 2c\cos\theta \{(R_2 + R_1)^2 - 4R_1R_2\}^{\frac{1}{2}}$$
$$= 4c^2 \cos\theta (\cos^2\theta - 1 + s^2)^{\frac{1}{2}}.$$



$CP_1 = CP_2 = CA = a$, $SC = c$, $SA = c - a$, $SP_1 = R_1$, $SP_2 = R_2$,
$SM = \frac{1}{2}(R_1 + R_2)$, $ST^2 = c^2 - a^2$.

Figure 1.

Hence
$$F = \frac{8\pi\kappa m^2}{(1 - s^2)^2 c^2} \int_0^\alpha (\cos^2\theta - 1 + s^2)^{\frac{1}{2}} \cos^2\theta \sin\theta\, d\theta.$$

Make the substitution
$$\cos\theta = (1 - s^2)^{\frac{1}{2}} \cosh u. \qquad u$$

Then
$$F = \frac{8\pi\kappa m^2}{c^2} \int_0^{\frac{1}{2}y} \sinh^2 u \cosh^2 u\, du,$$

where
$$\tanh \tfrac{1}{2}y = s. \qquad y$$

Therefore
$$F = \frac{\pi\kappa m^2}{4c^2} (\sinh 2y - 2y) \qquad \text{.....(3·4).}$$

This is Rankine's formula.

To this result we must add the correction for the earth's field $\mathbf{E}_0$. The earth's field acting alone would produce uniform magnetization of intensity $\kappa\mathbf{E}_0$ in the sphere. It is well known that such a distribution of magnetization is equivalent to a magnetic doublet at the centre of the sphere, of moment $\frac{4}{3}\pi a^3\kappa\mathbf{E}_0$. The only component of this which will contribute to the attraction of S in the direction SC

is the component in the parallel direction. If the component of the earth's field
E_* along SC is E_* the additional attraction will be

$$\frac{4}{3}\pi a^3 \kappa E_* \cdot \frac{2m}{c^3} = \frac{8}{3}\pi\kappa m E_* s^3 \qquad \text{.....(3·5),}$$

since the effective component of the magnetic doublet is in the end-on position.

Taking the figures given by Rankine, viz.

$$c = 1{\cdot}80 \text{ cm.}, \qquad a = 1{\cdot}28 \text{ cm.}, \qquad m = 50 \text{ c.g.s. units},$$

and taking E_* to be 0·16 gauss, we have for the uncorrected value of the attraction

$$F = 8{\cdot}48 \times 10^3 \kappa \text{ dynes},$$

and the correction due to the earth's field is

$$F_* = 24\kappa \text{ dynes},$$

which amounts to less than $\frac{1}{3}$ per cent. Of course the correction can be reduced to zero by orienting the apparatus so that the line SC is perpendicular to the magnetic meridian.

§ 4. THE FORCE DUE TO DISTRIBUTED POLES

The poles of a bar magnet are not concentrated in two definite points but are distributed throughout the length of the magnet, and it is therefore necessary to correct Rankine's formula so as to allow for the spatial distribution of the poles. In the experimental arrangement adopted by Rankine the bar magnet was cylindrical, its axis was vertical, the centre C of the paramagnetic sphere was on a level with one end of the bar magnet, and the resultant horizontal force on the sphere was measured with a torsion balance. The poles of the magnet may be regarded as distributed along its axis, and it seems to be impossible to obtain any simple expression for the horizontal force unless the distance of the magnet from the surface of the sphere is large compared with the distance over which the poles are distributed. In these circumstances the force of attraction would be extremely small. If, however, the axis of the magnet is horizontal and passes through the centre of the sphere when produced, the problem becomes considerably simplified. It seems worth while to carry out the necessary calculations in this case as there is some hope that, with this modification of the experimental arrangement, Rankine's method may yield *absolute* values of susceptibility.

r, θ, ϕ It is convenient to use spherical polar co-ordinates (r, θ, ϕ) with the origin at the centre C of the paramagnetic sphere and the axis coinciding with the axis of
ζ the bar magnet. The potential due to a unit pole on the axis at a distance ζ from C is

$$(r^2 + \zeta^2 - 2r\zeta\cos\theta)^{-\frac{1}{2}} = \zeta^{-1} \sum_{n=0}^{\infty} (r/\zeta)^n P_n(\cos\theta), \quad (r < \zeta),$$

where $P_n(\cos\theta)$ is Legendre's function of order n. Hence, if the linear density of
$m(\zeta)$ the pole strength is $m(\zeta)$, the potential V_0 of the applied field is given by

$$V_0 = \sum_{n=0}^{\infty} c_n r^n P_n(\cos\theta),$$

c_n where

$$c_n = \int \zeta^{-n-1} m(\zeta)\, d\zeta \qquad \text{.....(4·1).}$$

The component of the applied field normal to the surface of the sphere is given by

$$H_0^{(n)} = -(\partial V/\partial r)_{r=a}$$
$$= -\sum_{n=0}^{\infty} nc_n a^{n-1} P_n(\cos\theta),$$

and the component parallel to the axis is given by

$$H_0^{(z)} = -(\partial V/\partial z)_{r=a}$$
$$= \{-\cos\theta\,(\partial V/\partial r) + \sin\theta\,(\partial V/r\partial\theta)\}_{r=a}.$$

Now
$$\left\{-\cos\theta\frac{\partial}{\partial r} + \sin\theta\frac{\partial}{r\partial\theta}\right\} r^m P_m(\cos\theta)$$
$$= r^{m-1}\{-m\cos\theta\,P_m(\cos\theta) + \sin\theta\,\partial P_m(\cos\theta)/\partial\theta\}$$
$$= mr^{m-1}P_{m-1}(\cos\theta),$$

in virtue of one of the standard recurrence formulae. Hence

$$H_0^{(z)} = -\sum_{m=1}^{\infty} mc_m a^{m-1} P_{m-1}(\cos\theta).$$

The total mechanical force on the sphere is

$$\kappa\int H_0^{(n)} H_0^{(z)}\,dS = 2\pi\kappa\int_0^{\pi}\sum_{m,n} mnc_m c_n a^{m+n} P_{m-1}(\cos\theta)\,P_n(\cos\theta)\sin\theta\,d\theta$$
$$= 4\pi\kappa\sum_{n=1}^{\infty}\frac{n(n+1)}{2n+1}c_n c_{n+1}a^{2n+1} \qquad \ldots\ldots(4{\cdot}2).$$

For a unit pole at a distance c from the origin — c

$$c_n = c^{-n-1},$$

and the expression for the force becomes

$$\frac{4\pi\kappa}{c^2}\sum_{n=1}^{\infty}\frac{n(n+1)}{2n+1}s^{2n+1},$$

where $s = a/c$. It may be verified that this is the expression in powers of s of the function — s

$$F(s) = \frac{\pi\kappa}{4c^2}\left\{\frac{4s}{(1-s^2)^2} - 2\log\frac{1+s}{1-s}\right\}$$
$$= \frac{\pi\kappa}{4c^2}(\sinh 2y - 2y), \quad (s = \tanh\tfrac{1}{2}y),$$

which appears in Rankine's formula (3·4).

In general it will be necessary to determine $m(\zeta)$, the linear density of the pole-strength, by experiment and to calculate the coefficients c_n (4·1), by numerical integration. The rapidity of the convergence of the series (4·2) given above for the total mechanical force can be estimated as follows. If the nearest point on the bar magnet is at a distance c from the origin then

$$c_n = \int\zeta^{-n-1}\,m(\zeta)\,d\zeta < m/c^{n+1},$$

where m is the total pole-strength. Now the nth term of the series is — m

$$\frac{n(n+1)}{2n+1}c_n c_{n+1}a^{2n+1} < \frac{m^2 a}{2c^3}(n+1)s^{2n}$$

where $s=a/c$. Hence the series converges at least as rapidly as the series

$$\sum_{n=1}^{\infty}(n+1)s^{2n}=(1-s^2)^{-2}-1 \qquad \text{.....(4·3).}$$

p Now the remainder after p terms of the series (4·3) is

$$R_p=\sum_{n=p+1}^{\infty}(n+1)s^{2n}=\frac{s^{2p+4}}{(1-s^2)^2}+(p+2)\frac{s^{2p+2}}{(1-s^2)} \qquad \text{.....(4·4),}$$

and the remainder after p terms of the series (4·2) cannot exceed this number. Taking, for example, the value of s used by Rankine,

$$s=0{\cdot}711, \qquad s^2\fallingdotseq\tfrac{1}{2},$$

$$(1-s^2)^{-2}-1\fallingdotseq 3 \quad \text{and} \quad R_{10}\fallingdotseq 0{\cdot}0127.$$

Thus the error involved in neglecting all terms after the 10th is less than 0·42 per cent. The preceding analysis appears to furnish the necessary correction for the finite spread of the poles, and to furnish it in a form which does not require too laborious a series of calculations.

§ 5. ACKNOWLEDGMENT

Finally, the author wishes to express his gratitude to Prof. Rankine for his continued interest and helpful criticism.

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612.843.21

THE RELATION BETWEEN THE APPARENT INTENSITY OF A BEAM OF LIGHT AND THE ANGLE AT WHICH THE BEAM STRIKES THE RETINA

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ABSTRACT. Stiles and Crawford recently observed that the efficiency of a pencil of light was much greater when it passed through the centre of the lens of the eye than when it traversed an outer segment. This result has been confirmed for three observers by use of the authors' subjective photometer, in which a method of binocular matching is employed. One or two suggestions as to the origin of the phenomenon are put forward; it is almost certainly associated with the angle of incidence of the light on the retina, which may have an inherent directional sensitivity.

§ 1. INTRODUCTION

Stiles and Crawford[1] showed recently that when a narrow pencil of light was transmitted through the pupil of the eye and came to a focus on the retina, the brightness of the patch varied according to the part of the pupil used. When the light was axial the brightness was a maximum, but as the distance from

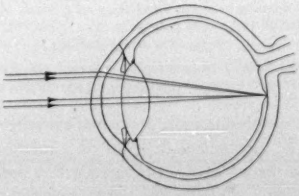

Figure 1. Cross-section of the eye, showing the path of an axial and an extra-axial pencil of light, each coming to a focus on the fovea.

the centre of the iris was increased the apparent brightness diminished. It can be seen at once from figure 1 that the axial beam corresponds to light incident normally on the retina, when the patch is being viewed on the fovea and the small eccentricity of the latter is neglected; while with the extra-axial beam, the greater the distance from the centre the more obliquely does the light strike the retina.

Stiles and Crawford obtained their results by a method of flicker photometry in which the reference beam was transmitted centrally through the pupil of the eye, and the test beam at various distances from the centre of the same eye. In the present case a different type of apparatus was available which, although not capable of the same accuracy as that used by Stiles and Crawford, gave a confirmatory set of curves which seemed worthy of publication.

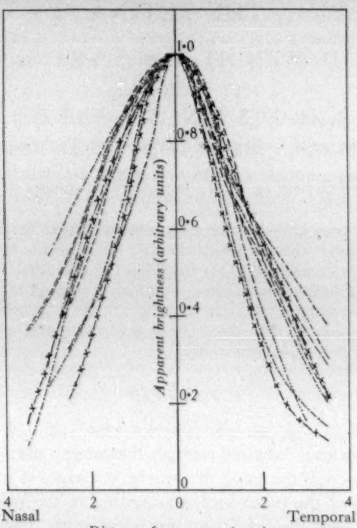

Figure 2. Curves showing relation between brightness of a beam of light and the distance from the centre of the iris at which the pencil enters the eye. Observer: W.D.W. Right eye.
White – – – – – –. Red –·–·–·–·–. Yellow –···–···–. Green –····–····–. Blue –×–×–×–.

§ 2. APPARATUS

The authors' subjective photometer, described elsewhere[2], was used to give the curves shown below. The instrument depends on a method of binocular matching in which a patch seen by the left eye is compared with a patch seen by the right eye. The left patch thus acts as a reference standard when the part of the pupil used in the right eye is varied.

§ 3. CONDITIONS OF OBSERVATION

Both eyes were dark-adapted for about 20 minutes before the observations were made, and comparison between the patches was made instantaneously and not by gazing continuously at the light. The diameter of the beam at the point where

it entered the eye was about 0·040 in., and the angular subtense of each patch seen on the retina was approximately $1\frac{1}{2}° \times 3°$. Only a horizontal traverse of the observer's pupil was possible. No attempt was made to increase the diameter of the pupil by the use of mydriatics.

§ 4. RESULTS

Observations were made by Dr R. J. Lythgoe and by the authors. Data for both white light corresponding to a colour temperature of about 2800° K., and colours selected by means of Ilford's spectrum filters, were obtained and the results

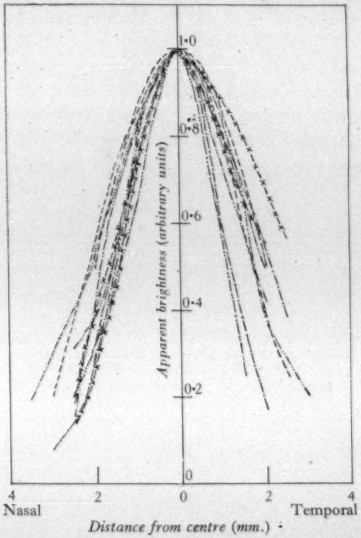

Figure 3. Curves showing relation between brightness of a beam of light and the distance from the centre of the iris at which the pencil enters the eye. Observer: J.H.N. Right eye. White ——. Red – · – · –. Yellow – · · – · · –. Green – · · · – · · · –. Blue – × – × – ×.

are shown in figures 2 to 4. The accuracy of observation was not high, the uncertainty of setting being of the order of 20 per cent. The spreading of the curves in figures 2 and 3, which include repeat observations, indicate the general reliability of the data.

§ 5. CONCLUSIONS

The mean curves for J.H.N., R.J.L., and W.D.W., figure 5, agree well with the data of Stiles and Crawford. These mean curves have been plotted in relation to the angle of incidence of the light on the retina, the angle being derived from the dimensions of an average eye. The magnitude of the effect is very striking and it is

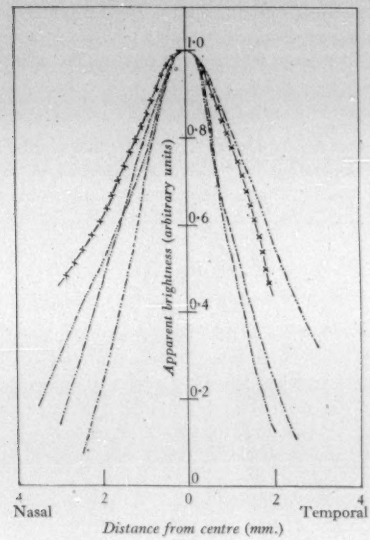

Figure 4. Curves showing relation between brightness of a beam of light and the distance from the centre of the iris at which the pencil enters the eye. Observer: R.J.L. Right eye.
Yellow –·–·–·–·–. Green –·····–·····–. Blue –×–×–×–.

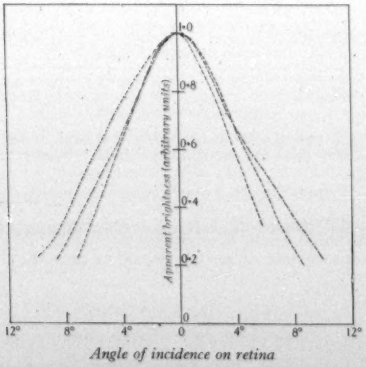

Figure 5. Mean curves showing the relation between the apparent intensity of a beam of light and the angle at which the beam strikes the retina.
W.D.W. –·–·–·–. J.H.N. –·····–·····–. R.J.L. –·····–·····–.

obvious that the loss of brightness cannot be due to any absorption in the optical media of the eye. The most plausible suggestion put forward by Stiles and Crawford was that absorption took place in the pigment epithelium assumed to have migrated between the rods and cones, and that this absorption varied according to the angle of incidence, since the light would have to pass through varying thicknesses of the pigment.

While this may be the true explanation, it is not, as Stiles and Crawford admit, very convincing. In view of the structure of the retina, it seems to us that the sensitive membrane may very well have a fundamental directional sensitivity. It may be, for instance, that the light has to enter directly into a cone in order to produce a photochemical reaction. The irregular orientation of the cones might then explain the curves obtained. Alternatively the light may be totally reflected inside the walls of the cone, and when the angle of incidence becomes too great the light escapes outside the cell and is inactive. These suggestions are only guesses, but they illustrate the possibility that the phenomenon may be the result of a fundamental process in the retina.

§ 6. ACKNOWLEDGMENTS

We should like to express our thanks to Dr Lythgoe for his assistance in making some of the observations and to the Medical Research Council for their financial support.

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551.585.2

THE USE OF THERMOCOUPLES FOR PSYCHROMETRIC PURPOSES

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ABSTRACT. The paper deals with certain factors affecting the use of thermocouples for psychrometric purposes, and considers some of the advantages possessed by instruments of this type. An investigation is made for the purpose of determining the manner in which the wet-bulb depression depends on the degree of ventilation, the diameter of the wire, the thickness and length of the water film covering the junction of the wet thermocouple, and the relative positions of the wet and dry thermocouples. It is shown that the need for forced ventilation of the wet thermocouple decreases as the diameter of the wetted wire is diminished. A typical example is given showing that for a psychrometer composed of nichrome and constantan wires of 40 s.w.g. mounted in a still air enclosure, the percentage relative humidity derived from its readings is only two or three units greater than that given by a fully ventilated instrument, when psychrometric tables appropriate to the latter condition are used in each instance.

§ 1. INTRODUCTION

In the course of some experiments in which very fine thermocouples were used to measure the distribution of vapour pressure in air streaming over a wet surface, it was found that relatively low air-velocities were sufficient to give the maximum depression of the wet bulb, and that in the complete absence of forced ventilation the depression of the wet bulb was within a few per cent of this maximum depression. It is clear that the diminished importance of adequate ventilation gives thermocouple psychrometers a great advantage over mercury-in-glass wet and dry thermometers. The necessary observations can also be obtained more quickly when thermocouples are used to measure humidities than when the dew-point method is employed, and the fact that smaller convection currents are set up is a further advantage in experiments where undisturbed air conditions are required.

The above experiments were first made early in 1933, but a subsequent search of the literature revealed that a few months earlier mention had been made elsewhere of the small amount of ventilation required by thermocouple psychrometers. References to these papers are included in the next section. The present paper deals with several factors which become of importance in the application of thermoelectric methods for psychrometric purposes.

§2. PRIOR REFERENCES TO THERMOCOUPLE PSYCHROMETERS

In 1929 E. Griffiths, J. R. Vickery and N. E. Holmes[1] used a psychrometer consisting of thirty-three wet and dry copper-constantan thermocouples connected in series, as a means of observing from a distance the relatively small wet-bulb depressions obtained in cold-storage holds on board ship. The wet junctions were each fitted with a muslin sleeve, comparable in size with the bulb of a clinical thermometer, and in consequence an air-speed of the order of 3 metres per second was needed to give the maximum depression.

M. Okada[2], in making a study of air circulation in cold-storage warehouses, used thermocouples to measure the distributions of both temperature and humidity set up in a rectangular chamber cooled above and heated below. J. H. Lanning[3] records the use of wet and dry copper-constantan thermocouples to measure the relative humidity in desiccators, the smallness of the quantity of water vapour introduced into the enclosure being considered an advantage.

R. Hilpert[4], in his experimental determination of the evaporation and heat-transfer from a vertical plate in still air, used a manganin-constantan thermocouple of 0·15 mm. wire to measure the humidity of the air. The wet and dry thermocouples, surrounded by radiation shields, were mounted in a tube through which a slow stream of air passed before entering the experimental enclosure. The wet junction could be moistened as required by water forced from a small capillary tube by heating air in a closed upper space. Hilpert studied the effect of air-velocity on the depression of this psychrometer, and gives a curve showing the maximum depression to be produced by a velocity of only 20 cm./sec.

At about the same time H. Wald[5] and L. Ketternacker[6] also advocated the use of very fine wire thermocouples as a means of reducing the necessity for artificial ventilation, and published similar theoretical support. V. Rossi[7] has employed thermocouples in a study of the temperature and humidity gradients in the atmosphere, whilst K. Schropp[8] has recently employed this means of measuring humidities in an experimental investigation of the factors governing the formation of frost and dew on cooling tubes.

E. J. Blades[9] has used an analogous method for the determination of the vapour pressure of a solution, the sample being in the form of a drop and retained in a loop formed at the junction of a thermocouple composed of very fine wires.

§3. THEORY DUE TO KETTERNACKER

Ketternacker derives the following expression for the ratio of the observed to the maximum difference in temperature between the wet and dry thermometers, on the assumption that the Joule heat developed within the wire and the radiation thereto can be neglected:

$$a=\frac{(T_a-T_0)}{(T_a-T_\omega)}=1\Big/\left\{1+\frac{\pi}{2}\sqrt{(\alpha_D d^3)}\,(\sqrt{\lambda_1}+\sqrt{\lambda_2})\Big/\alpha F\left[1+\frac{r}{C_p}\left(\frac{dx}{dT}\right)_{T=T_\omega}\right]\right\}, \qquad a$$

where T_a is the dry-bulb temperature, T_0 the observed wet-bulb temperature,

T_ω the fully ventilated wet-bulb temperature, d the diameter of the wire, λ_1 and λ_2 are the thermal conductivities of the metals composing the wires, α_D is the surface emissivity of the wire, F the area of the moist surface, r the latent heat of vaporization of water, C_p the specific heat of air, α the coefficient of heat-transfer from air to surface, and $(dx/dT)_{T=T_\omega}$ the change in saturated water-content of the air with change of temperature at T_ω.

The tables for use with a fully ventilated wet-and-dry-bulb thermometer can be used to give the true relative humidity from readings obtained with a thermocouple psychrometer when the value of a is unity. It will be seen that in the foregoing expression a tends towards this value as α is increased, as the thermal conductivity of the wire is decreased, and as the diameter approaches zero. In the usual type of psychrometer α is increased by means of forced ventilation, but since α also increases as the diameter decreases, the foregoing equation shows clearly that the need for forced ventilation becomes less as the diameter of the wire is decreased.

§ 4. DESCRIPTION OF EXPERIMENTS

Selection of thermocouple elements. The metals chosen for the two thermocouple elements were nichrome and constantan, which in the neighbourhood of room-temperature have a somewhat greater e.m.f. per degree than the copper-constantan combination more frequently employed, and further possess relatively low thermal conductivities, that of nichrome being about 0·03 c.g.s. unit and that of constantan being 0·06 c.g.s. unit.

Comparison between thermocouples and mercury thermometers. Two thermocouples were made up of 40-gauge nichrome and constantan wires joined end to end. In order to retain the moisture on the wet thermocouple the wire of this thermocouple was wrapped with very fine cotton for a distance of about a centimetre on each side of the junction. These thermocouples were mounted in a wind tunnel in which ordinary wet and dry mercury-in-glass thermometers were also suspended. Observations of the wet-bulb depressions were made on both types of psychrometer, and also on a fully ventilated Assmann psychrometer, and the values of a were determined for the unventilated condition and for wind speeds of 65 and 260 cm./sec. The values of a for these three air conditions were 0·80, 0·95 and 0·99 for the mercury thermometers, and 0·97, 0·99$_5$ and 1·00 for the thermocouples. This result shows clearly that the provision of forced ventilation is of far less importance when fine wire thermocouples are used than in the case of mercury-in-glass thermometers.

The thermocouple psychrometer possesses the further advantage that it reaches its equilibrium temperature in a few seconds, whereas the wet thermometer takes several minutes.

Tests with thermocouples of various diameters. A number of thermocouples were prepared, by using nichrome and constantan wires of 14, 18, 26, 32 and 40 s.w.g., the two elements being butt-welded together. A covering of fine cotton was wrapped over each thermocouple so as to extend for a distance of 5 cm. on each side of the

junction of the two wires. Observations were made of the wet-bulb temperature indicated by each of these thermocouples in the absence of forced ventilation, and in a draught sufficient to produce the maximum depression of the wet bulb. The former condition is referred to in this paper by the designation "still air". The results obtained are set out in table 1, a being the ratio of the still-air depression to the maximum depression. The air-temperature was approximately 18° C., and the relative humidity varied from 35 to 40 per cent.

Table 1. Results obtained with thermocouples of various diameters

Wire gauge (s.w.g.)	Diameter of wire (cm.)	Depression in still air (°C.)	Maximum depression (°C.)	a
14	0·202	6·35	7·20	0·88
18	0·12	7·15	7·85	0·91
—	—	5·28	5·86	0·90
26	0·045	5·80	6·15	$0·94_3$
32	0·028	6·62	6·89	$0·95_7$
40	0·017*	5·81	6·02	$0·96_3$
40	0·012	6·00	6·10	$0·98_4$

* Wires doubled back and twisted together.

The true wet-bulb reading is given when $a=1$, and it is seen from figure 1 that the departure from this value is proportional to the square root of the diameter

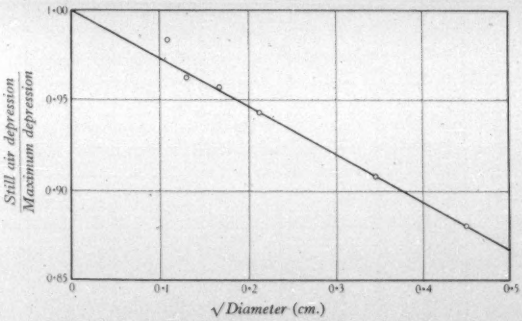

Figure 1. $\frac{\text{Still air depression}}{\text{Maximum depression}}$, against square root of diameter of wire.

of the wire. This result is indicated by Ketternacker's theory, if α is assumed to be independent of the diameter. This agreement is presumably fortuitous, since α, the coefficient of heat-transfer, is known to increase rapidly as the diameter diminishes.

Investigation into the effect of the thickness of the cotton covering. A few measurements have been made for the purpose of showing the extent to which the depression of the wet thermocouple is dependent on the thickness of the cotton covering.

A number of 40-gauge thermocouples were prepared having their junctions covered with cotton of various thicknesses, and were tested in a manner similar to that already described. The results obtained are set out in table 2, from which it will be seen that value of a decreases in an approximately linear manner with increase in cotton-thickness.

Table 2. Results obtained with cotton coverings of various thicknesses

Thickness of cotton (cm.)	Depression in still air (°C.)	Maximum depression (°C.)	a
0·045	7·50	7·93	$0{\cdot}94_6$
0·024	7·62	7·93	$0{\cdot}96_1$
0·010	5·58	5·79	$0{\cdot}96_3$
0·009	7·73	7·98	$0{\cdot}96_9$
0·007	7·65	7·87	$0{\cdot}97_2$
0·0015	7·70	7·86	$0{\cdot}98_9$

The influence of the length of cotton covering on the wet-bulb depression. Tests of a similar kind were carried out to ascertain how the wet-bulb depression depended on the length of wire that was covered by cotton and thus kept wet. The cotton covering was wound to equal distances on each side of the junction, and two sizes of wire were examined in this way, namely the 26 and 18 s.w.g. It will be seen from the results plotted in figure 2 that total coverings extending over a length of at

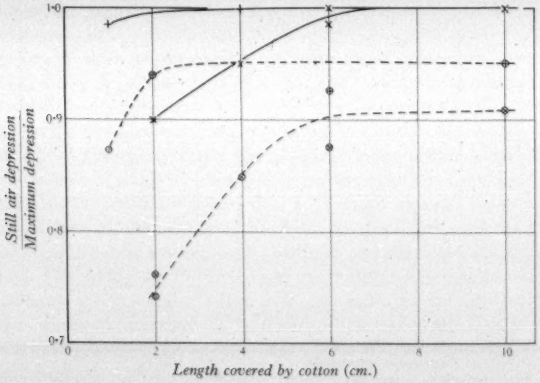

Figure 2. Influence of cotton covering on a. ⊗ 18 s.w.g. still air; × 18 s.w.g. air speed 250 cm./sec.; ⊕ 26 s.w.g. still air; + 26 s.w.g. air speed 250 cm./sec.

least 3 and 6 cm. are required in these respective cases to ensure the maximum values of a being reached. For 40-gauge wire a wrapping over a length of about 1 cm. appeared to be sufficient, but results with shorter lengths were not obtained.

It will be observed from the curves in the figure that when the length of wetted wire was less than the above value even the maximum degree of ventilation used in

these experiments was insufficient to give a a value of unity. It would appear from this that unless the wire is wetted for a sufficient length on both sides of the junction, even strong ventilation does not lead to true values for the relative humidity. A similar result would probably hold good for any form of wet-bulb thermometer.

Calibration of a thermocouple psychrometer for use in an unventilated enclosure. It has already been shown that provided the wet thermocouple is composed of very thin wires the relative humidity deduced from its depression in still air is within a few per cent of the true humidity. The calibration of such a thermocouple psychrometer, which has been used for the measurement of the relative humidity of a closed chamber, will now be described.

This psychrometer was constructed from 40-gauge wires, and consisted of wet and dry thermocouples differentially connected together and a separate dry thermocouple. The instrument was mounted in a closed chamber, the two dry thermocouple junctions being alongside each other and in a position where they were not influenced by the cooler wet thermocouple. The relative humidity of the air in the chamber was varied from about 20 per cent to saturation, and readings were observed of the dry temperature and depression of the wet bulb, as given by the differential thermocouple, both when the air-movement was due to natural convection only, and when the air was vigorously stirred by means of a fan driven by an external motor. This forced ventilation was sufficient to give the maximum depression of the wet thermocouple, and by comparing these values with those obtained in the absence of ventilation a calibration for the latter condition is obtained.

The results are given in table 3, psychrometer tables compiled for an adequately ventilated instrument being used for both ventilated and unventilated conditions.

Table 3. Relative humidities given by thermocouple psychrometer when unventilated and when fully ventilated

Dry-bulb reading (°C.)	Wet-bulb reading		a	Relative humidity	
	fully ventilated (°C.)	unventilated (°C.)		true (per cent)	unventilated (per cent)
22·00	10·93	11·30	0·97	21	24
21·74	11·37	11·78	0·96	25	28
21·72	11·90	12·38	0·95	29	32
20·98	11·26	11·70	0·94	28	30
20·82	13·26	13·70	0·94	41·5	45
20·37	15·55	15·82	0·94	61	62·5
20·68	17·10	17·35	0·93	70	72
20·72	18·50	18·70	0·88	81	83
21·12	20·20	20·43	0·75	92	94
22·02	21·64	21·75	0·72	97	97·5

It will be seen that the values of a are somewhat smaller than those previously given for wire of this size. The still-air values in the latter case had been obtained in an open-ended wind tunnel situated in a large room, and it is probable that

there was relatively more air-movement in this instance than in the closed chamber used in the present tests. Over the greater part of the humidity-range, however, the values obtained for the relative humidity from the readings of the unventilated instrument are only some two or three units too great.

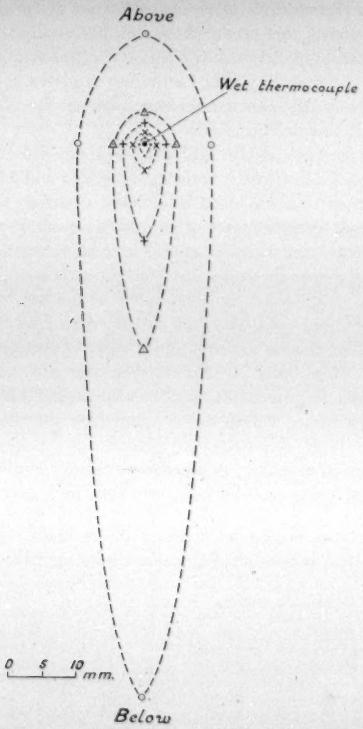

Figure 3. Isothermals around a wet horizontal thermocouple in still air. Humidity 52 per cent. Dry thermocouple reading decreased by ⊙, 0° C.; ⊛, 0·6° C.; +, 1·2° C.; ×, 2·4° C.; •, 3·6° C. Depression of wet thermocouple, 6·1° C.

Considerations regarding the location and requisite distance apart of the wet and dry thermocouples. One advantage which the thermocouple psychrometer possesses over hygrometers of other types is that its small size permits local variations in humidity to be studied. In making such a determination, the two temperature-measurements should be made in positions as close together as is consistent with avoidance of the errors likely to arise from mutual interference of the thermocouple readings. When the humidity is being determined by a ventilated thermocouple

psychrometer the wet and dry thermocouples need not be more than a millimetre or two apart, provided that the dry thermocouple is situated to windward of the wet thermocouple.

In unventilated conditions a separation of about ten times this distance is essential to prevent the dry-bulb reading from being influenced by the cool air surrounding the wet bulb. Figure 3 indicates the extent to which the reading of the dry thermocouple is lowered, when this element is parallel to the wet thermocouple and at various distances above, below, or to either side of it. It will be observed that the effect of the stream of cold air falling from the wetted surface persists to a considerable distance, and care should be taken to ensure that the dry thermocouple shall not be placed within this region.

§ 5. ADVANTAGES AND APPLICATIONS OF THERMOCOUPLE PSYCHROMETERS

Apart from the present purposes for which thermocouple psychrometers have been found to be well suited, namely the measurement of the humidity-gradient above a moist surface either with or without forced ventilation, and as an alternative to the dew-point method of determining the humidity of a still-air enclosure, this type of instrument possesses many other possible spheres of application. When, for instance, the air under test is very dry, the large amount of cooling required by a dew-point thimble before the dew point is attained makes the determination by this means laborious, and thermocouples may be preferred. The rapidity of the response of a thermocouple, which permits fluctuations in humidity to be detected, has already been mentioned. This type of psychrometer also possesses the normal advantages of the thermoelectric methods in that the instrument is distant-reading, and can easily be made recording. It could also readily be adapted as a method of humidity-control by the employment of some such device as that suggested by R. M. Zabel and R. R. Hancox[10], in connexion with the use of thermocouples as a means of controlling furnace-temperatures.

Multi-element thermocouples or those composed of elements with a large temperature coefficient of voltage would be of considerable service in vapour-pressure measurements in which a high sensitivity is required, for instance measurements near saturation or at low temperatures.

§ 6. ACKNOWLEDGMENTS

The above investigation formed part of an item of research conducted at the National Physical Laboratory on behalf of the Engineering Committee of the Food Investigation Board, and the author desires to express his thanks to this Committee for permission to publish an account of the results obtained. Acknowledgment is also made to Mr M. J. Hickman for assistance with the experimental work.

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THERMAL DIFFUSION IN DEUTERIUM MIXTURES

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ABSTRACT. With the object of comparing the molecular fields of hydrogen and deuterium, the thermal diffusion effects[1] in mixtures of hydrogen-nitrogen and of deuterium-nitrogen have been measured over a temperature-range $-190°$ to $+100°$ C. It appears that deuterium has the same type of field as hydrogen. Helium-nitrogen mixtures, which are of interest because the mass ratio is the same as in deuterium-nitrogen mixtures, were also examined.

§ 1. INTRODUCTION

Measurements of thermal diffusion in gas mixtures have given information about the nature of molecular fields of force[2,3]. The amount of thermal separation due to a temperature-gradient from T_1 to T_2 is found, in accordance with Chapman's theory[1], to be generally proportional, except at low temperatures, to $\log(T_1/T_2)$; thus the separation may be expressed as $k_t \log(T_1/T_2)$. The ratio of the quantity k_t thus experimentally determined to the value $k_{t\infty}$ calculated for the particular case in which the molecules behave like rigid elastic spheres has been termed the *thermal separation ratio* R_t. If the molecules are point centres of force varying inversely as the qth power of the distance, then R_t may be regarded as an approximate measure of the index q. Values of q have been determined for many gases, and reasonable agreement with values deduced by other methods is found.

The method has now been applied to a comparison of the molecular fields of hydrogen and deuterium. It was convenient for this purpose to compare the thermal separation in a series of hydrogen-nitrogen and deuterium-nitrogen mixtures. Helium-nitrogen mixtures were also examined. These are interesting because helium has the same mass as deuterium but a different electronic structure; this is just the converse of the case of hydrogen and deuterium.

The experiments fall into two parts: (1) measurements of thermal separation in mixtures of varying proportions, two fixed temperatures being used; these are the room-temperature T_2 and the steam-temperature T_1. From the experimental values of k_t and the theoretical values of k_t for rigid elastic spheres, the value of R_t over this temperature-range is calculated. (2) Measurements of thermal separation with varying temperature-differences. In this case T_1 is the room-temperature and T_2 varies from room-temperature down to $-190°$ C.

It has previously been found[2] that R_t for hydrogen-nitrogen mixtures is constant at temperatures above $-80°$ C. but that at lower temperatures its value diminishes. This result has been interpreted as showing that a diminution in the index of the repulsive force occurs as the temperature decreases. It is of interest therefore to compare the extent of the change in R_t for deuterium-nitrogen mixtures with that in hydrogen-nitrogen mixtures.

§ 2. METHOD

Preparation of the deuterium. The deuterium was prepared by distilling in a vacuum about 0·2 cm.^{3} of heavy water on to clean sodium. Two samples were prepared: the first from water containing about 96 per cent of deuterium, the second from water containing 98 per cent.

A complication arises from the presence of HD and H_2 molecules. Sample 1 had a deuterium-content of 92 per cent, and consisted therefore of 84 per cent of D_2, 15 per cent of HD, and 1 per cent of H_2.* Sample 2 had a deuterium-content of 96 per cent D_2 and 4 per cent HD. As a first approximation it is sufficient to regard the mixture of D_2, HD, and H_2 as a simple gas whose molecular weight is the weighted mean of its constituents. Any thermal diffusion effect between these molecules themselves will certainly be too small to detect.

The separation measurements. The thermal separation was measured with apparatus essentially similar to that described in earlier papers.

For the first part of the work a steam-jacketed bulb with a capacity of about 4 cm.^{3} was attached to the katharometer, one cell of which thus formed the cold side at room-temperature. The factor for the conversion into total separation of the change in concentration measured by the katharometer was determined by means of separate experiments with common gas mixtures for which the experimental values of k_t were already known. The three sets of mixtures, H_2-N_2, D_2-N_2 and He-N_2, were each examined over a wide range of concentration under identical conditions.

The measurements at low temperatures were made with the apparatus previously used for the rare gases[2]. The temperatures, however, were measured by a pentane thermometer instead of the thermocouple. The thermometer was checked against a similar thermometer calibrated at the Reichsanstalt.

§ 3. RESULTS

The variation of separation with concentration. Figure 1 shows the variation of separation with concentration when $\log_{10}(T_1/T_2)=0{\cdot}112$. Sample 1 of deuterium was used in this part of the work.

The thermal separation occurring in a mixture is a function of the mass, size and proportions of the two kinds of molecules as well as of the molecular fields. The thermal-separation ratio, however, depends only on the molecular forces, and it is this quantity which must be evaluated for a comparison of the fields of hydrogen

* For the analysis of the deuterium we are indebted to Dr Farkas.

and deuterium. It is defined as the ratio of k_t experimentally determined as d(separation)/d(log T), to the value $k_{t\infty}$ calculated for molecules behaving like rigid elastic spheres. This calculated value is derived from Chapman's expression involving the masses, sizes and proportions of the two kinds of molecules. When numerical values for the mass and size are inserted, a comparatively simple expression for $k_{t\infty}$ in terms of the proportions is obtained. Such expressions have already

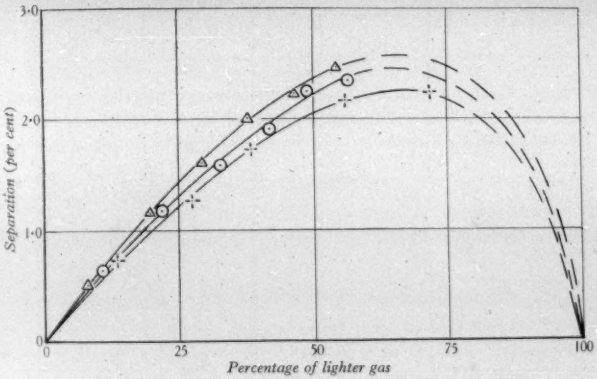

Figure 1. Variation of separation with concentration when $\log_{10} T_1/T_2 = 0{\cdot}112$, $T_1 = 100°$ C., and $T_2 = 14°$ C. ⊙ H_2-N_2; ⊹ D_2-N_2; ⊿ He-N_2.

been given for hydrogen-nitrogen and helium-nitrogen mixtures[2]. For deuterium-nitrogen the expression for k_t as calculated for rigid elastic spheres is as follows:

$$k_{t\infty} = \frac{5}{2}\,\frac{0{\cdot}274n_1 + 0{\cdot}286n_2}{1{\cdot}817n_1/n_2 + 0{\cdot}733n_2/n_1 + 2{\cdot}667},$$

where n_1 is the proportion by volume of nitrogen, n_2 the proportion by volume of deuterium, and $n_1 + n_2 = 1$. In the calculation, the molecular diameter of deuterium was taken as being equal to that of hydrogen: the viscosity measurements of Cleave and Maass[5], published while this work was in progress, show this to be justified. The above expression applies to pure deuterium of mass 4; a modification was necessary to take account of the slightly smaller *mean* mass of the deuterium sample 1. n_1, n_2

The mean value of R_t over the range of concentrations examined was found to be as shown in table 1.

Table 1. Values of R_t and q

Mixture	R_t	q
H_2-N_2	0·59	11
D_2-N_2	0·58	11
He-N_2	0·65	12·5

The error in determining R_t is about 2 per cent. The difference between the values for hydrogen-nitrogen and deuterium-nitrogen is thus within the experi-

mental error, and we may conclude that at normal temperatures the deuterium molecule has a force-field similar to that of the hydrogen molecule.

R_t for the helium-nitrogen mixture is definitely greater than for the hydrogen-nitrogen or deuterium-nitrogen mixtures. The helium molecule, having the same mass as deuterium, is thus clearly shown to have a different field, being in fact harder than deuterium.

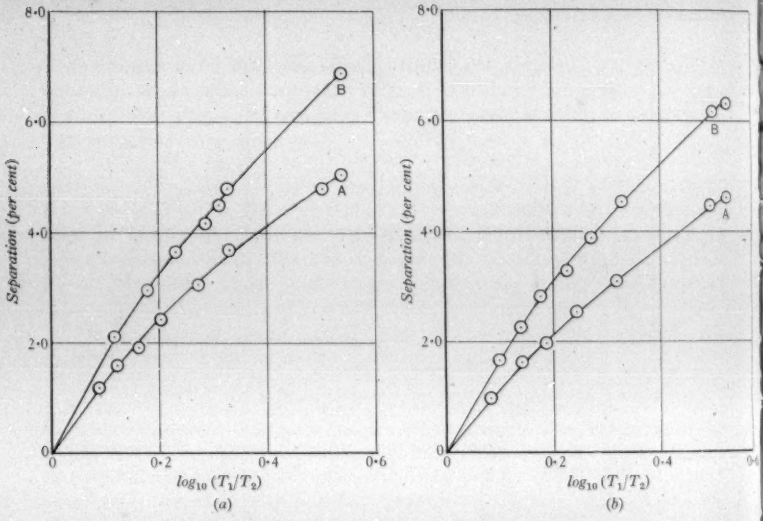

Figure 2. The variation of thermal separation with $\log(T_1/T_2)$ when $T_1 = 10°$ C., $T_2 = 0° \rightarrow -190°$ C. (*a*) Hydrogen-nitrogen; A, 28·0 per cent and B, 42·7 per cent of hydrogen. (*b*) Deuterium-nitrogen; A, 28·1 per cent and B, 42·6 per cent of deuterium.

The third column of table 1 gives the values of the index q of the repulsive force, as found by interpolation in a series of corresponding values of R_t and q given by Chapman and Hainsworth[10]. These values apply to the special case when the mass and size ratios are very large, but the extension to the present case is unlikely to affect them greatly.

The variation of separation with temperature at low temperatures. The thermal separation occurring in mixtures of hydrogen-nitrogen and deuterium-nitrogen was measured as the cold-side temperature T_2 varied from room-temperature to −190° C. Two mixtures of deuterium-nitrogen were examined: one containing 42·6 per cent of deuterium and the other 28·1 per cent. These were compared with two hydrogen-nitrogen mixtures in which the proportion of hydrogen was the same as that of deuterium in the deuterium-nitrogen mixtures. The results are shown in figure 2.

It is seen that in deuterium-nitrogen mixtures, as in hydrogen-nitrogen mixtures, there is a departure at low temperatures from the linear relation between separation and log (T_1/T_2): that is, R_t is again a function of the temperature. In table 2 the

Table 2. Variation of R_t with temperature

Mixture	0° C.	−70° C.	−95° C.	−125° C.	−150° C.
H_2-N_2	0·57	0·57	0·45	0·39	0·36
D_2-N_2	0·58	0·58	0·45	0·38	0·34

values of R_t at different temperatures for the 42·6-per-cent-deuterium mixture are compared with those for the corresponding hydrogen mixture. The experimental values of k_t at different temperatures are obtained from the slope of the {separation, log (T_1/T_2)} curves and R_t is obtained as before from the ratio of the experimental and theoretical values of k_t.

There is no significant difference at any temperature between the values for the deuterium-nitrogen mixture and those for the hydrogen-nitrogen mixture.

§ 4. CONCLUSION

The results* show that the thermal separation ratio R_t is the same for deuterium-nitrogen mixtures as for hydrogen-nitrogen, both at normal temperatures and at low temperatures where R_t depends on the temperature. This means that, while the thermal separation in the deuterium mixtures is less than in the corresponding hydrogen mixtures, the difference is entirely accounted for by the difference in mass of the molecules. Consequently the fields of force of hydrogen and deuterium molecules appear to be similar. This is in agreement with the results obtained by Cleave and Maass[5], who compared the viscosities of hydrogen and deuterium over a wide range of temperatures.

On the other hand, although the masses of the deuterium and helium molecules are the same, the thermal separation in helium-nitrogen mixtures is greater than in corresponding deuterium-nitrogen mixtures. The difference must here be attributed to a difference in the molecular fields.

§ 5. ACKNOWLEDGMENTS

We thank Prof. S. W. J. Smith for kindly providing facilities for this work in the Physics Department of the University of Birmingham; Dr T. L. Ibbs for advice and criticism; and Dr F. P. Bowden for a supply of deuterium oxide.

* An interesting paper by O. and G. Blüh[6] has recently appeared in which are described thermal diffusion measurements made by means of an optical method. There is general agreement with similar measurements made by the katharometer method in this Department, except at low temperatures. There seems however to be an error in the method used by O. and G. Blüh for calculating the total separation from the observed change in concentration, and when this is corrected the low-temperature values agree well with those obtained[2] by Ibbs and one of us (K. E. G.). This concordance of results obtained by entirely independent methods is gratifying.

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THE ACCURATE DETERMINATION OF IONOSPHERIC EQUIVALENT HEIGHTS

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ABSTRACT. A method has been described for measuring the equivalent height of an ionized region of the upper atmosphere with an accuracy of $\pm 0{\cdot}5$ km. It has been shown that though the accuracy is of this magnitude the resolving-power of the apparatus, which is fixed by the width of the pulse used, is not so great, there being difficulties in determining the height difference of two pulses less than 5 km. apart. However, when certain precautions are taken it is possible to obtain height separations of the order of 5 km. with a fair degree of accuracy. With the aid of the apparatus described it has been shown that there are no sudden changes of height in either the E_1 or the F_2 region greater than those which might be expected from errors of measurement. The equivalent height of the so-called "abnormal E" region has been compared with that of E_1 and is shown to be not more than 3 or 4 km. greater. The frequency separation of the two critical frequencies for the ordinary and the extraordinary rays returned from the abnormal E region has been measured and is shown to be in agreement with the value to be expected on the magneto-ionic theory of the propagation of waves through an ionized medium. A discontinuity in the curve of height against frequency has been shown to exist at a frequency just less than 2 Mc./sec. This phenomenon, which was first noticed by Naismith at Slough two years ago, is shown to have all the characteristics of penetration and leads to the inference that there is a secondary maximum of ionization a few kilometres below the maximum of the E_1 region, somewhat similar to the ledge on the F region discovered by Appleton. For purposes of reference in the paper this maximum is called E_s. It has been shown that the height of the E_1 region is less in winter than in summer but that the diurnal variation of height shows a minimum of height several hours after midday. It is suggested that the winter minimum is due to a general increase in molecular density in the atmosphere caused by the lower temperatures of winter time.

§ 1. INTRODUCTION

Experimental investigations of the ionization of the upper atmosphere by means of wireless waves have resulted, after ten years of work, in the demonstration of the existence of two regions of ionization of sufficient density to produce reflection of waves of radio frequency. These are now known as the "E" and the "F" regions and close observation has established the presence of a subsidiary maximum of ionization on the lower side of the F region, which in England is apparent only in summer and in the daytime. There is also fairly detailed and accurate knowledge of the behaviour of this region in relation to variation of frequency of the propagated wave, time of day, time of year and, to a

E, F

certain extent, variation of latitude. The behaviour of the *E* region is not known with such accuracy, as the variations of equivalent height which it undergoes are much smaller than those of the upper *F* region.

In measurements of equivalent height by means of the frequency-change method of Appleton[1] or the echo method of Breit and Tuve[2] the accuracy which is normally obtained is in the neighbourhood of ± 2 km. In the case of the frequency change method a change of 16 kc./sec. when the *E* region has an equivalent height of 100 km. produces 10 fringes representing *P'*, i.e. 200 km., the sender and receiver being near together. Thus to measure with an accuracy of ± 2 km. it is necessary to estimate one-fifth of a fringe, which is about the limit for a reliable estimate. In the case of the echo method with a cathode-ray oscillograph, the usual time base has a scale in which 10 mm. correspond to an equivalent height of about 50 km.; the diameter of the cathode-ray spot is more than 0·5 mm., so that the accuracy cannot be more than $\pm 0{\cdot}5$ mm., which represents $\pm 2{\cdot}5$ km., and is sometimes less. With the use of a Duddell oscillograph greater accuracy can be obtained, but large quantities of film are needed and the observations cannot be made at frequent intervals, so that the use of that instrument has not been very extensive.

The purpose of this research has been to investigate the behaviour of the *E* region in greater detail than has been usual, by increasing the accuracy of the measurement of the equivalent height.

§ 2. APPARATUS

It was decided that the simplest way of obtaining greater accuracy was to increase the length of the time base on a cathode-ray oscillograph, disposing successive short lengths of it one below the other, and to take frequent snap photographs of the echo pattern in order to obtain a faithful record of quick variations of equivalent height. A description of such a type of time base for use in television scanning[3] gave a basis for construction, and in collaboration with Dr O. O. Pulley a suitable circuit was designed. The wiring diagram is given in figure 1. A 250-volt supply charges condenser C_1 through a variable resistance r_3. When the voltage has risen to a critical value as set by the grid bias on the gas-filled relay T_1, C_1 is discharged by the relay into condenser C_2. Condenser C_2 has a much greater capacity than C_1,* so that C_1 is practically completely discharged. The second terminal of C_2 is earthed and the potential variations of the two condensers are amplified by single stages of resistance-capacity amplification and applied, that of C_1 to the *X* axis plates of the oscillograph and that of C_2 to one of the *Y* axis plates. The relay T_1 has its anode earthed through a similar relay T_2 while condenser C_2 is shunted by a power valve (A.C.P.). The grids of these last two components are connected in parallel through a resistance to a square form oscillation of fifty cycle frequency. Thus for half a cycle the grids are positive, the two condensers are virtually short circuited and the spot remains stationary on the

* The values are as follows: $C_1 = 0{\cdot}05\ \mu$F., $C_2 = 2{\cdot}0\ \mu$F.

oscillograph screen. For the other half of the cycle the grids are negative and the long time scale is traced, forming a pattern as shown in figure 2 (*a*). By varying the resistance r_3 the charging rate of condenser C_1 can be varied, thus opening or closing the scale, while variations in the grid bias of the relay T_1 change the maximum voltage of C_1 and thus vary the length of each section of the time base. This is of great value when an echo happens to occur just at the end of a section, for a small change in the setting of the potentiometer r_4 will bring the echo properly on to that section and enable the equivalent height to be measured easily.

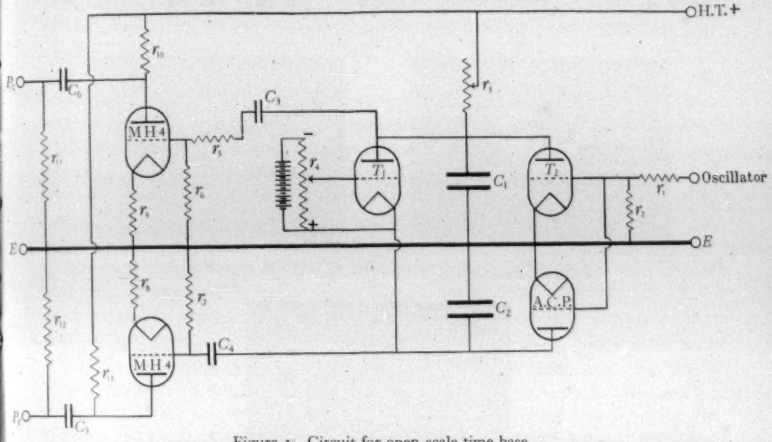


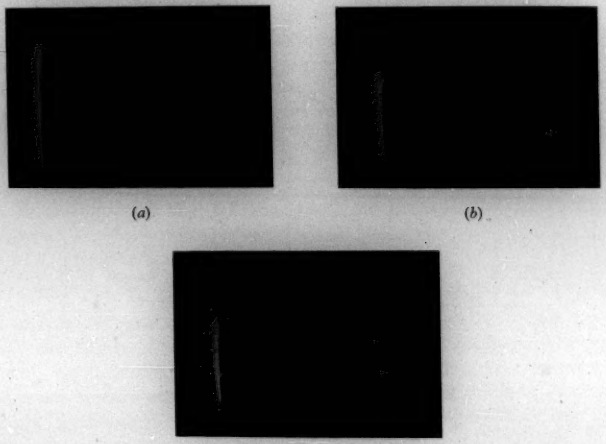
Figure 1. Circuit for open-scale time base.

The square-form oscillation was obtained from the oscillator in the time-base device usually used for the measurement of echo times. This oscillator could be locked in synchronism with the incoming pulse so that the ground-ray pulse was kept stationary at the beginning of the scale[4]. Usually the values of C_1 and r_3 were so arranged that 50 mm. on the time base represented 50 km. of equivalent height; thus measurement to the nearest millimetre gave an accuracy of $\pm 0{\cdot}5$ km.

It will readily be realized that on such an open scale the pulse will be very broad, and as it is not possible to increase the gain of the receiving set proportionally, the rise of the front edge of the pulse will be slow and it will be difficult to make measurements accurately, if the foot of the pulse is taken as a reference point as is usual. It was just at the time when the apparatus was being constructed that O. O. Pulley, in a letter to *Nature*[5], drew attention to the possibility of using the first differential of the voltage variation which forms the pulse to obtain the position of the peak of the pulse instead of the foot. A circuit such as he described was fitted by him to the receiving set, and figure 2 (*c*) shows the type of oscillographic record which was obtained. In figure 2 (*a*) is seen the time base with no signal

impressed; the small deflections mark off successive intervals of 50 km. In figure 2 (*b*) is shown the effect of impressing a pulse in the normal way, to illustrate the difficulty of observing the beginning of the pulse accurately. In figure 2 (*c*) the first differential of the pulse has been impressed. Here it is quite easy to fix the position of the peak of the pulse, for at that point the trace crosses the zero line at a definite angle instead of becoming asymptotic to it as in the previous case.

For recording purposes the trace in the tube was photographed with a film camera on standard cinematograph film so arranged that after each exposure of half a second the film was moved on through a distance equivalent to one frame by a ratchet device. This mechanism could be driven by a motor either at the rate



(*a*) (*b*)

(*c*)

Figure 2.

of four exposures per minute or at the rate of one exposure every ninety seconds. If desired it could be operated by hand so as to take a photograph at any desired moment.

In order to measure the equivalent heights an auxiliary apparatus was constructed. This consisted of a brass frame in which the developed film could be slid under a square aperture of the same size as the frame aperture of the camera. Above this aperture was fixed a transparent positive of a photograph of standard millimetre graph paper taken with the film camera. A mirror directed light through both films, and the two were observed through a simple microscope with a magnification of about 3×. The positive formed a graticule of reference, the time marks on the trace gave intervals of 50 km., and by interpolation the equivalent height for each photograph could be determined quite quickly.

§ 3. OBSERVATIONS

The first use to be made of the apparatus was to search for sudden variations of equivalent height of both the *E* and the *F* regions, of a magnitude too small to be detected readily with apparatus of less accuracy. A number of runs on a constant frequency were taken for the *F* region, exposures being made every quarter of a minute. These runs showed a continuous variation of height with time, but there was no sign of any sudden change of height of the order of 4 km., what variation there was being of about the magnitude of the estimated experimental error. Observations at constant frequency on the *E* region gave slightly different results. The height generally remained constant, there being a slow change of a few kilometres in the space of 4 to 5 hours. While on some days the curve was practically a straight line with no variations greater than 1 km. due to experimental error, on other days there were quite large variations in an interval of 1 minute, some of the height-changes being as great as 10 km. Observations over a range of frequencies (generally called "a $P'-f$ run") showed that these changes occurred when the extraordinary component of the ray returning from the *E* region had an amplitude comparable with that of the ordinary component. When the extraordinary component was strongly absorbed, the height-variation was not greater than the magnitude of the experimental error, except for the slow change over a period of several hours.

A theoretical examination of the effect of the superposition of one pulse upon another with a very small time difference between them shows that the resultant is a single pulse as long as the two components are almost in phase, but that a change of amplitude or phase of either component produces a change in the position of the peak of the resultant. For example, where it is assumed that the pulse has the form $y=1+\cos\theta$ and the separation of the two components is one-tenth of a pulse-width, a change in amplitude of one of the components from zero to unity (i.e. to equality with the other component) will cause the peak of the resultant pulse to move one-twentieth of a pulse-width. In the case of a pulse whose width on the time scale is 50 km. this will mean a shift of 2·5 km. On the other hand if the two components should be out of phase and comparatively close together, the resultant is two pulses with a separation greater than the true separation of the components, one pulse being larger than the other unless the two components are equal in magnitude. Thus it happens that when the echo-amplitude of the extraordinary ray is smaller and exactly out of phase with the ordinary echo, a single peak is seen whose apparent equivalent height may be a tenth of a pulse-width greater or smaller than the true equivalent height. In general the situation is that while it is possible to obtain accuracy of determination of equivalent height with a value of $\pm 0{\cdot}5$ km. it is not possible to obtain a resolving power of anything like that figure, as this depends on the width of the pulse which in its turn is set by the frequency band-width which can be used in the receiving set.

In addition to observations on a steady frequency, occasional observations ($P'-f$ runs) were taken at noon over a range of frequency, the variation being

made in steps of about 0·05 Mc./sec., so that a graph of equivalent height against frequency could be plotted. These were for the purpose of investigating the *E* region only and so were not continued beyond that frequency at which the echo from the *E* region disappeared. During the period from June to November 1934 thirty-six such graphs were plotted and from them information has been gained

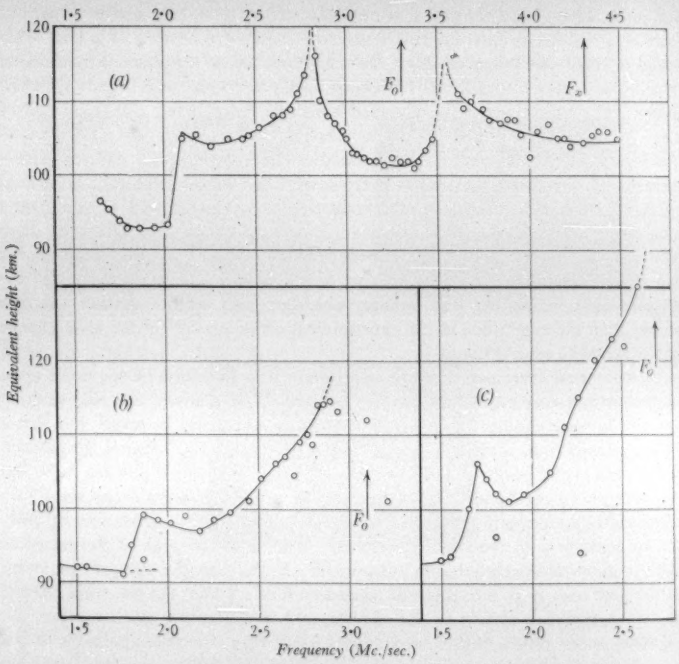


Figure 3. (*a*) August 28; (*b*) September 12; (*c*) October 12; Noon G.M.T.

under four heads. Three of the graphs have been reproduced in figure 3 as they illustrate most of the features to be discussed.

Usually, as the frequency is increased the equivalent height remains constant for a while, after which there is an increase accompanying the penetration of the region. Presently region *E* is penetrated and then reflection takes place from region *F*: see figures 3 (*b*) and 3 (*c*) where the appearance of the *F* echo is indicated by an arrow. On some days, especially in the summer, after penetration has taken place reflection continues from the *E* region, the equivalent height decreases, and for a time echoes

are observed from both regions; see figure 3 (*a*). This phenomenon has been called by E. V. Appleton "abnormal *E*"[6] and must be due to some form of partial reflection caused by a very steep gradient of ionic density somewhere in the region. O. O. Pulley noticed in 1933 that this hump in the equivalent {height, frequency} curve sometimes repeated itself about 0·7 Mc./sec., and suggested that it was caused by the extraordinary component of the downcoming wave repeating the behaviour of the ordinary component. In the curves plotted with the open-scale time base this double hump has been observed quite often, and a table is given below showing the frequencies at which the equivalent height of the *E* region became a maximum and those at which the ordinary and the extraordinary components of the ray returning from the *F* region began to be received.

abnormal *E*

Table 1

Date	$f_{(\max.1)}$ (Mc./sec.)	$f_{(\max.2)}$ (Mc./sec.)	$f_{E_1}^{o}$ (Mc./sec.)	$f_{E_1}^{x}$ (Mc./sec.)	$f_{\max.2}-f_{\max.1}$ (Mc./sec.)	$f_{E_1}^{x}-f_{E_1}^{o}$ (Mc./sec.)
June 13	3·6	3·8	3·6	4·2	0·2	0·6
14	2·95	3·65	3·4	4·2	0·7	0·8
15	3·1	3·9	3·5	4·2	0·8	0·7
20	3·3	4·1	3·8	4·7	0·8	0·9
22	3·3	4·1	4·1	4·7	0·8	0·6
Aug. 14	3·0	3·9	3·3	4·2	0·9	0·9
15	2·9	3·6	3·2	4·2	0·7	1·0
20	2·9	3·8	3·2	3·8	0·9	0·6
24	3·1	3·7	3·4	4·6	0·6	1·2
27	3·0	3·5	3·4	4·3	0·5	0·9
28	2·8	3·7	3·3	4·3	0·9	1·0
Sept. 11	2·9	3·5	3·1	4·2	0·6	1·1
15	2·7	3·5	3·0	No data	0·8	—
Oct. 19	2·8	3·3	2·9	No data	0·5	—
				Mean values	0·69	0·86

In the columns from the second to the fifth are given in order the frequencies at which *E* reached its first and second maximum heights and at which the ordinary and extraordinary components of *F* began to appear. These second two frequencies have been taken as the critical frequencies for the *E* region and have been labelled as such; the first two frequencies are simply called $f_{(\max.1)}$ and $f_{(\max.2)}$. In every case except one in this table it will be seen that the ordinary ray began to be returned from the *F* region after the first maximum height in the *E* region has been observed but before the second maximum height had occurred. Thus although it was not possible to obtain the state of polarization of the *E* echo at various parts of the curve, there is little doubt that the first maximum corresponds to penetration of the *E* region by the ordinary ray while the second maximum is due to penetration by the extraordinary ray. As further evidence the figures in the sixth column may be taken. These are the differences between the two frequencies for maximum height, and their mean value is 0·69 Mc./sec., a figure which is quite in agreement with the frequency separation to be deduced from the magneto-ionic theory of wave-propagation.

$f_{(\max.1)}$, $f_{(\max.2}$

After penetration of the E region has taken place the decreasing equivalent height of the abnormal E region can be explained in terms of the decreasing retardation in E region. As the frequency is increased above that for which the μ is nearly zero and the group velocity is very small, the retardation gradually decreases and the equivalent height returns to normal. Now however it must be assumed that the point in the region at which reflection is taking place is not necessarily the lower boundary of the E region, but may be some very steep ionization gradient which produces a partial reflection of the wave, since the F-region echo is simultaneously observed.

In order to get some idea of the position of this sudden change of ionic density the equivalent heights were measured on the curves, first at low frequencies where it seemed probable that the equivalent height represented almost the lower boundary of the region, being unaffected either by penetration of the layer or by group retardation of the wave, and secondly at the highest frequencies, where the curve had once again become flat, the reflection being partial now and the group retardation negligible. It was not possible to do this for all the curves where abnormal E was present, for sometimes the echoes faded out before the curve became sensibly flat again, so only part of the thirty-six curves is represented in table 2.

Table 2

Date	Equivalent height of E_1 region (km.)	Equivalent height of abnormal E (km.)	Height of abnormal E less height of E_1 (km.)
June 13	102	102	0
14	108	103·5	−4·5
22	104	110	6
July 2	103	106	3
16	98	101	3
17	99	108	9
Aug. 15	99	100	1·5
27	102	107	5
28	105	105	0
Sept. 6	94	95	1
18	95	103	8
Oct. 18	91	90	−1
19	100	100	0
19*	95	95	0
29†	95	95	0
Nov. 21	92	92	0
Mean values	98·87	100·78	1·9

* 11.0 G.M.T. † 13.0 G.M.T.

This table shows that except in two cases the abnormal E region is at the same height as the normal E or a few kilometres higher. If it is true that the echo is due to some form of partial reflection at a surface of discontinuity, then the height measured will be a true height except for such group retardation as may remain in consequence of the final frequency of reflection not being sufficiently above the critical frequency for E. On the other hand the height measured for normal E is an equivalent height and therefore somewhat greater than the true height of the

region. The result is to indicate that the abnormal E region is always at a greater height than the lower boundary of the E region and therefore cannot be identified with an increase of the ionization-gradient at the lower boundary. It is apparently a steep gradient within the layer itself.

One new phenomenon which has been demonstrated by these $\{P', f\}$ curves is the presence of a discontinuity in equivalent height at a frequency lower than the critical frequency for the ordinary ray returned from the E region. This is shown quite clearly in the curves of figure 3 together with the fact that the discontinuity is accompanied by group retardation and presents all the characteristics of penetration of an ionized region. In addition there is evidence in two of the curves, and in others not shown, that, after the discontinuity, reflections from the smaller equivalent height, which may be due to an extraordinary ray, are recorded. At the time when this phenomenon was being further investigated, information was received from Mr Naismith at the Radio Research Station, Slough, that since early in 1933 a peculiarity had been observed in the $\{P', f\}$ curves at frequencies round about 2 Mc./sec. This took the form of an apparent group-retardation phenomenon, but the accuracy of the apparatus was not sufficient to determine if there was really any change of height or not. During a visit to Slough the curves taken at the Halley Stewart Laboratory were compared with those taken at Slough and it seemed quite definite that the phenomena being observed at the two places were the same, the frequencies being in agreement with one another. In addition the Slough curves showed a repetition of the phenomenon at a frequency about 0·7 Mc./sec. higher than the first. This bears out the suggestion that the first discontinuity is due to penetration by an ordinary component of the returning ray while the second corresponds to penetration by the extraordinary component. At the Halley Stewart Laboratory, where the noise-level is higher than at Slough, though it is possible to observe the ordinary component the extraordinary component is generally too weak through absorption to give a visible echo except at values of set-gain made impossible by noise. Some of the information bearing on this suggestion is summarized in table 3. In the columns from the second to the fourth are shown the critical frequency for this suggested region, which must be similar in nature to the F_1 shelf below the F_2 region, and will be provisionally referred to as E_s; the critical frequency for the ordinary ray returned from the E_1 region; and the difference between these two frequencies. In the last three columns are given the mean equivalent height for frequencies between 1·5 Mc./sec. and the critical frequency for the E_s region, the mean height for frequencies between that and 2·3 Mc./sec. and the difference between these two heights. These figures show that the critical frequency for this region bears a fairly constant relation to that for the E region, being about 0·9 Mc./sec. below it, while the equivalent height is about 5 km. lower than that of the E region. E_s

A previous argument applies to a certain extent here, for while the equivalent height of the E_s region is probably not accompanied by group retardation, there is a possibility that the height of the E region is increased owing to group retardation in the E_s region. Thus the difference of height may very well be too large, and one

would regard 2–3 km. as about the right figure. This makes the heights of normal E_1, abnormal E, and E_s all lie within a range of 6 or 7 km. of equivalent height and agrees with previous observations on the E region that variations of ionic density take place over much smaller height-ranges in the E region than in the F region. One cannot help associating this with the results of many theoretical considerations, to the effect that variations of pressure with height are greater at 100 km. than at 200 km.

In figure 4 the equivalent-height data of table 3 have been plotted to bring out the nature of another phenomenon, the variation of equivalent height with time of year. This figure shows that the heights of both the E_1 and the E_s regions were greatest in the summer and became less as the winter advanced. This is a variation

Table 3

Date	f_{E_s} (Mc./sec.)	$f_{E_1}^0$ (Mc./sec.)	$f_{E_1}^0 - f_{E_s}$ (Mc./sec.)	Mean height 1·5 Mc./sec. to f_{E_s} (km.)	Mean height f_{E_s} to 2·3 Mc./sec. (km.)	Increase of height (km.)
July 17	1·7	2·8	1·1	97	99	2
Aug. 20	1·85	2·9	1·05	99	102	3
24	1·9	3·1	1·2	99	102	3
27	2·05	3·0	0·95	97	102	5
28	2·05	2·8	0·75	95	105	10
29	2·25	3·0	0·75	98	106	8
Sept. 10	1·9	3·1	1·2	90	95	5
12	1·9	2·9	1·0	92	98	6
15	1·7	2·7	1·0	98	102	4
18	1·8	2·85	1·05	93	95	2
Oct. 12	1·7	2·6	0·9	95	101	6
17	1·7	2·65	0·95	93	102	9
19	1·8	2·8	1·0	95	100	5
19	1·9	2·65	0·75	94	95	1
23	1·7	2·5	0·8	90	97	7
Nov. 6	1·9	2·7	0·8	95	97	2
8	1·7	2·45	0·75	93	106	13
		Mean values	0·93			5·3

in a sense opposite to that experienced by the F_2 region and requires some amendment of current theory for its explanation. Chapman has given an explanation of the well-known shape of the {ion-density, height} curve as due to the fact that the intensity of the ionizing agent (ultraviolet light) increases with altitude while the pressure of the air (molecular density) decreases with height[7]. Various theoretical estimates of the pressure-variation with height indicate that up to 100 km. (the height of the E region) the decrease in pressure per kilometre rise is large, while above 100 km. this rate of decrease is much smaller[8]. At the place where the pressure begins to rise comparatively steeply with decrease of height a sudden stop will be put to the effectiveness of free electrons in affecting the refractive index for radio-frequency waves by a quick decrease in their mean free paths. Thus the lower boundary of the E_1 region will coincide very nearly with the position of this

bend in the {pressure, height graph}. A drop in temperature of the atmosphere as a whole will move the position of this bend towards the earth and produce a decrease in the equivalent height of the E_1 region. It might be expected that if this is the case for variations of temperature throughout the year it would also be true for variations during the course of a day. A number of continuous observations of equivalent height have been carried out with rays of constant frequency from sunrise to sunset on certain days in order to investigate this possibility. It was necessary of course to make sure that the height observed was the true equivalent height and was not increased at any time by penetration or group retardation, and for this purpose the steady frequency was made as low as possible and on several occasions during the day $P'-f$ runs were made in order to ascertain if the equivalent {height, frequency} curve was flat at the frequency in use. In the curves the penetration associated with the appearance of the echo at sunrise and its

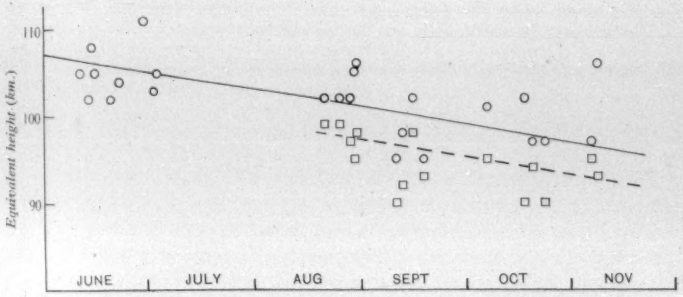


Figure 4. Equivalent height of the ionosphere. ○, region E; □, region E_s.

disappearance at sunset can be seen, but during the intermediate hours, when the true equivalent height of the region was being measured there was a decrease of height towards the middle of the day followed by an increase towards sunset. The position of the minimum of height was not always at midday but was sometimes $1\frac{1}{2}$–3 hours later. This result is not entirely contradictory of the suggestions advanced above, for the variations in temperature of the whole of the atmosphere above a given point on the earth are not likely to immediately follow the altitude-changes of the sun but will have an appreciable lag. This lag may be so large a fraction of the 24-hour period of the earth's rotation that the pressure-variation may be almost in opposition to the intensity variation of the ultraviolet light, so as to flatten out the {equivalent-height, time} curve, or else to distort it. The latter process seems to be the case in the curves where the time of minimum height is later than midday. On the other hand, the very slow change of mean day temperature from summer to winter will be faithfully followed by the whole of the atmosphere and so give a minimum of equivalent height in winter.

§ 4. ACKNOWLEDGMENTS

The author desires to express his indebtedness to Prof. E. V. Appleton for suggesting this work and giving much valuable assistance and advice, and also to Dr F. W. G. White and Dr O. O. Pulley for help in the design of circuits and many useful suggestions as the work proceeded.

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ON THE DEVELOPMENT OF THE QUANTUM EQUATION AND A POSSIBLE LIMIT TO ITS APPLICATION

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ABSTRACT. The first-order equation of the quantum theory is developed by applying a parallel displacement to the matrix length of a vector. The quantum theory reveals itself as a law of parallel displacement from which a modification of Weyl's theory is deduced. In this modification a term containing the mass of a charged particle occurs as well as terms containing the charge and electromagnetic potential. The principle of minimum proper time emerges from this result as a limitation of the application of the quantum equation to a particle in an electromagnetic field.

§ 1. INTRODUCTION

THE suggestion that the quantum theory may be regarded as a manifestation of a particular form of natural metric was made some time ago[1]. It was shown that Schroedinger's equation could be regarded as a condition satisfied by a particular metrical function described as a scale factor and that it led directly to a modification of Weyl's theory. In the latter the measured lengths of physics are subject to changes upon undergoing parallel displacements, the magnitudes of the changes being dependent on the path of displacement. According to Weyl the changes of length are related to the components of electromagnetic potential and the non-integrability of the change corresponds to the same property of this potential. But if the theory in this form be applied directly to the space and time of physics, it leads to a curious result. One would conclude that atoms must emit spectral lines of a frequency dependent upon the potential of the field in which they are situated. In the course of time, since atoms occupy very different fields, there would be no lines of a definite frequency from differently placed atoms. In discussing this fact Weyl took the point of view that his parallel displacement was of the nature of an ideal process and that his metrical field could not be directly defined as a result of measurements with instruments. If we have to take this view with regard to it, the theory seems to be robbed of physical content.

But the theory of parallel displacement, when we modify it by recognizing it as manifested in the quantum theory, recovers its physical content, for it makes the change of length periodic with the path of displacement. The quantum paths of the theory of Bohr and Sommerfeld are those for which the change goes through a

complete number of periods and the displaced vector recovers its original length. The shortest length over which such a recovery is possible is h/m_0c when a particle of rest mass m_0 is occupying the path of the displacement. By a different procedure London[2] reached the same conclusion in a contribution to the subject which was especially designed to remove the artificial element inherent in Weyl's explanation of his point of view.

m_0

Since these suggestions were first made, the quantum theory has developed considerably and the first-order equation has been introduced by Dirac together with matrices of a fundamental character not unlike that possessed by axes of coordinates. In spite of the radical change in the form of the theory which results, the conviction that the branch of physics here concerned is a metrical manifestation has grown and has been gradually given a more satisfactory form of expression than was previously possible. It has become evident that the fundamental equation of the theory is of the nature of a law of parallel displacement. The development of the equation from a simple geometrical idea becomes possible, the idea requiring for its expression the concept of a matrix length.

In a recent contribution[3] to this question a somewhat general development has been given, that it appears that a simpler theory is possible and that it leads to unification of the microscopic and macroscopic domains of physics.

It is our present purpose to give an account of this theory.

§ 2. MATRIX LENGTH AND PARALLEL DISPLACEMENT

We make the supposition that the measured length of a vector having a typical component A_m is represented in the theory by l where

A_m, l

$$l = \alpha^m A_m \qquad \ldots\ldots(1),$$

α^m, m

α^m denotes a typical fundamental matrix, and m may have the values 1–4. A set of four such matrices is associated with each point and they are to be regarded as possessing the character of vectors and to be functions of the coordinates.

This length may be regarded as a fundamental element of microscopic physics or of matrix geometry. Mimura[4] who has also introduced this idea speaks of the geometry as "wave geometry". An important link between this geometry and what we may describe as macroscopic geometry is a relation due, in the first place, to Tetrode. This relation will be expressed in the form

$$\alpha^m \alpha^n = g^{mn} I + s^{mn} \qquad \ldots\ldots(2).$$

I, s^{mn}

I is the unit matrix and s^{mn} is the antisymmetric part of the product $\alpha^m \alpha^n$. It corresponds to the spin matrix of the quantum theory. The components g^{mn} are the gravitational components of the theory of relativity and thus we have in equation (2) a link between the quantum theory and the theory of relativity or, as we may say, between microscopic and macroscopic physics. When a vector A_m undergoes a parallel displacement, it is understood that its components change by an amount dA_m given by

dA_m

$$dA_m = \Delta_{mn}{}^{l} A_l dx^n \qquad \ldots\ldots(3).$$

$\Delta_{mn}{}^{l}$ is undetermined, but we shall interpret it by means of the equation $\Delta_{mn}{}^{l}$

$$\Delta_{mn}{}^{l} = \Gamma_{mn}{}^{l} + T_{mn}{}^{l} \qquad \text{.....(4),}$$

where $\Gamma_{mn}{}^{l}$ is the Christoffel bracket expression and $T_{mn}{}^{l}$ will be restricted in accordance with the requirements of the physical theory. This means that certain limitations will be placed upon it by the quantum theory and by the theory of electromagnetism. $\Gamma_{mn}{}^{l}$, $T_{mn}{}^{l}$

From equation (1)

$$dl = \left(\frac{\partial \alpha^{p}}{\partial x^{m}} + \Delta_{nm}{}^{p}\,\alpha^{n}\right) A_{p}\,dx^{m} \qquad \text{.....(5)}$$

$$= K_{m}{}^{p}\,A_{p}\,dx^{m},$$

where the matrix $K_{m}{}^{p}$ denotes the expression in the bracket. $K_{m}{}^{p}$

§ 3. THE INVARIANT LENGTH

In accordance with an earlier suggestion made in connexion with Weyl's theory of electromagnetism, we shall suppose that each point of space is provided with a scale factor. This is a function of the coordinates and in the present case it is a matrix ψ, which we suppose to consist of a single column of values ψ_{1n}, where n can have the values 1 to 4, the other components of the matrix being zero. It is convenient to denote the components ψ_{1n} by ψ_{n} for simplicity. ψ, n ψ_{n}

This matrix combined with the matrix l produces a matrix of invariant length L, thus L

$$L = l\psi.$$

The invariance refers to a parallel displacement, so that

$$dL = 0,$$

$$d\,(l\psi) = dl\psi + ld\psi = 0.$$

From equation (5) $$\left(\alpha^{p}\,\frac{\partial \psi}{\partial x^{m}} + K_{m}{}^{p}\,\psi\right) A_{p}\,dx^{m} = 0.$$

If this relation is to be true for all vectors and for all displacements, it follows that

$$\alpha^{p}\,\frac{\partial \psi}{\partial x^{m}} + K_{m}{}^{p}\,\psi = 0 \qquad \text{.....(6).}$$

This equation is in the form of a mixed tensor and if we write $p = m$ and sum over all values of m, we obtain through the process of degeneration of a tensor

$$\alpha^{m}\,\frac{\partial \psi}{\partial x^{m}} + K_{m}{}^{m}\,\psi = 0 \qquad \text{.....(7).}$$

But although this equation follows from equation (6), the converse is not true.

§ 4. COMPARISON WITH THE QUANTUM EQUATION

This equation is of the same form as Dirac's equation which forms the basis of the quantum theory and is the only means we have of approaching the problems of atomic physics. The development of equation (7) from a simple geometrical and metrical idea reveals the quantum equation as the manifestation of this concept

in the world of physics. We expect to obtain from physics some information about the form of $K_m{}^p$. Actually a comparison with the quantum equation gives us the form of $K_m{}^m$, the degenerated form of $K_m{}^p$.

Dirac's equation is

$$\alpha^m \frac{\partial \psi}{\partial x^m} - \frac{2\pi i e}{hc} \phi_m \alpha^m \psi + \frac{2\pi i m_0 c}{h} \alpha_0 \psi = 0 \qquad \text{.....(8).}$$

e This equation is applied to a particle of rest mass m_0, carrying a charge e, in an ϕ_m electromagnetic field with potential components ϕ_m and, if we make use of equation (2), we can add "in a gravitational field".

α_0 The matrix α_0 is additional to the matrices α^m, and in Dirac's theory it must satisfy the relations

$$\left.\begin{aligned} \alpha^m \alpha_0 + \alpha_0 \alpha^m &= 0 \\ \alpha_0{}^2 &= 1 \end{aligned}\right\} \qquad \text{.....(9).}$$

These five matrices are essential in the theory and they must be linearly independent.

We adopt the relations (9) together with (2). The equations (7) and (8) become identical if $K_m{}^m$ be chosen as follows:

$$K_m{}^m = -\frac{2\pi i e}{hc} \phi_m \alpha^m + \frac{2\pi i m_0 c}{h} \alpha_0 \qquad \text{.....(10).}$$

This means that at any point of space the law of parallel displacement, as it is expressed by equation (7), is determined by ϕ_m, the mass m_0 and an additional matrix α_0.

From equations (4), (5) and (10) we deduce

$$\frac{\partial \alpha^m}{\partial x^m} + \Gamma_{nm}{}^m \alpha^n + T_{nm}{}^m \alpha_n = -\frac{2\pi i e}{hc} \phi_m \alpha^m + \frac{2\pi i m_0 c}{h} \alpha_0 \qquad \text{.....(11).}$$

When both gravitational and electromagnetic fields are absent, the term in $m_0 c$ in equation (8) still persists. In this case the α^m are constants and the $\Gamma_{nm}{}^m$ and ϕ_m vanish so that

$$T_{nm}{}^m \alpha^n = \frac{2\pi i m_0 c}{h} \alpha_0 \qquad \text{.....(12).}$$

§ 5. RECONSIDERATION OF THE FORMULA FOR CHANGE OF LENGTH

This introduces a difficulty for it means that α_0 is not linearly independent of the α^n. It is true that the $T_{nm}{}^m$ may contain an arbitrary function which will introduce the necessary element of freedom in another way. But this procedure leads to complications and it seems desirable to remove the difficulty by other means. We must introduce α_0 into equation (7) independently of the $T_{nm}{}^m$. There is an obvious way of doing this by means of the α^m. These matrices are like axes of coordinates and it is reasonable to suppose that in using them as reference matrices at different points we must have some particular method in relating them as we pass from one

point to another. It is somewhat as if we had a parallel displacement of the matrices. Thus we might adopt the following expression for the change of α^m as a result of a parallel displacement:

$$\Delta\alpha^m = -\delta_n{}^m\, a\,\alpha_0\,\Delta x^n \qquad \text{.....(13).}$$

We use this form of expression since it is our intention to make it as simple as possible, in accordance with our requirements in the quantum theory. Thus $\delta_n{}^m$ will have the value 1 when $m=n$, otherwise it is zero. Clearly a more general theory is possible with $\delta_n{}^m\,\alpha_0$ as a more general matrix $\Lambda_n{}^m$. a is a constant which we shall fix later.

$\delta_n{}^m$

a

We can say that the matrices (α^m) are equal at two points when they have the values (α^m) and $(\alpha^m+\Delta\alpha^m)$ at these points respectively. Thus in passing from one point to the other α^m undergoes the change $\partial\alpha^m/\partial x^n$ on account of the change of coordinates, and since $\Delta\alpha^m$ is the change required when the matrix sets are regarded as equal, the total change in passing between the two points is

$$\left(\frac{\partial\alpha^m}{\partial x^n}\,\Delta x^n - \Delta\alpha^m\right), \text{ equal to } \left(\frac{\partial\alpha^m}{\partial x^n} + \delta_n{}^m\, a\,\alpha_0\right)\Delta x^n.$$

This procedure suggests that there is some additional variation in the α^m in passing along the line between the two points which is not accounted for by simply considering the four coordinates (x^m). We shall return to this point later after applying this new variation to the change of length.

Returning now to equation (5) and taking account of this new element of variation, we obtain instead of that equation

$$dl = \left(\frac{\partial\alpha^p}{\partial x^m} + \delta_m{}^p\, a\,\alpha_0 + \Delta_{nm}{}^p\,\alpha^n\right) A_p\, dx^m \qquad \text{.....(14)}$$

$$= K_m{}^p\, A_p\, dx^m,$$

where $K_m{}^p$ has now the value given by

$$K_m{}^p = \frac{\partial\alpha^p}{\partial x^m} + \delta_m{}^p\, a\,\alpha_0 + \Delta_{nm}{}^p\,\alpha^n \qquad \text{.....(15).}$$

Thus by equation (8) although $K_m{}^p$ retains the same value, when we pass to the quantum equation, the term in α_0 is no longer associated with $T_{nm}{}^m$. We have now

$$\frac{\partial\alpha^m}{\partial x^m} + \Delta_{nm}{}^m\,\alpha^n = -\frac{2\pi i e}{hc}\,\phi_m\,\alpha^m \qquad \text{.....(16)}$$

instead of equation (11).

The matrix α_0 has an independent place in the theory, being concerned with matrix displacement. The quantum equation requires

$$\delta_m{}^m\, a\,\alpha_0 = \frac{2\pi i m_0 c}{h}\,\alpha_0 \qquad \text{.....(17),}$$

and since summation is implied,

$$4a = \frac{2\pi i m_0 c}{h} \qquad \text{.....(18).}$$

§ 6. AN IMPORTANT RELATION

From equation (2) we obtain Tetrode's relation

$$2g^{mn} = \alpha^m \alpha^n + \alpha^n \alpha^m,$$

whence

$$2\frac{\partial g^{mn}}{\partial x^l} = \frac{\partial \alpha^m}{\partial x^l}\alpha^n + \alpha^m \frac{\partial \alpha^n}{\partial x^l} + \frac{\partial \alpha^n}{\partial x^l}\alpha^m + \alpha^n \frac{\partial \alpha^m}{\partial x^n}$$
$$= (K_l{}^m - \delta_l{}^m\, a\, \alpha_0 - \Delta_{rl}{}^m\, \alpha^r)\,\alpha^n + \text{etc.}$$

by equation (15).

If we remember the relation (4) and the identity satisfied by the gravitational components g^{mn} together with equation (9), we obtain

$$2\,(g^{rn}\, T_{rl}{}^m + g^{rm}\, T_{rl}{}^n) = (K_l{}^m\, \alpha^n + \alpha^n\, K_l{}^m) + (K_l{}^n\, \alpha^m + \alpha^m\, K_l{}^n) \quad \ldots\ldots(19).$$

This determines the part of $g^{rn}\, T_{rl}{}^m$, which is symmetrical in m and n, in terms of the parallel displacement matrix $K_l{}^m$.

§ 7. CHANGE OF LENGTH IN MACROSCOPIC SPACE DURING A PARALLEL DISPLACEMENT. MODIFICATION OF WEYL'S THEORY

The square of the length of a vector with components A_m is determined in the theory of relativity by

$$l^2 = g^{mn}\, A_m\, A_n \quad \ldots\ldots(20).$$

On account of Tetrode's relation this can be regarded as the square of the matrix length, since

$$l^2 = \alpha^m\, A_m\, \alpha^n\, A_n = g^{mn}\, A_m\, A_n,$$

the antisymmetric part of $\alpha^m\, \alpha^n$ dropping out in this case. In a parallel displacement of the vector A_m, we obtain a change of length given by

$$\delta l^2 = \left(\frac{\partial g^{mn}}{\partial x^l} + \Delta_{rl}{}^m\, g^{rn} + \Delta_{rl}{}^n\, g^{rm}\right) A_m\, A_n\, \delta x^l$$
$$= (g^{rn}\, T_{rl}{}^m + g^{rm}\, T_{rl}{}^n)\, A_m\, A_n\, \delta x^l \quad \ldots\ldots(21).$$

Thus it is the symmetrical part of $g^{rn}\, T_{rl}{}^m$ in m, n which determines the change in length, and by equation (19) this is determined by the matrix $K_l{}^m$.

Weyl's theory of electromagnetism consists in assigning a value to the expression in brackets in equation (21). He chose, in fact, the value $2g^{mr}\,\phi_l$ so that in his theory ϕ_l

$$\frac{\delta l^2}{l^2} = 2\phi_l\, \delta x^l$$

or

$$\frac{\delta l}{l} = \phi_l\, \delta x^l \quad \ldots\ldots(22).$$

In this equation l denotes the scalar length and is not, of course, a matrix.

It seems clear from equation (10) that in the present theory ϕ_l will be associated with the factor $2\pi ie/hc$, since the expression (19) relates $T_{rl}{}^m$ with the matrix $K_l{}^m$.

We thus identify the symmetrical part of $g^{rn}\, T_{rl}{}^m$ with $-(2\pi ie/hc)\, g^{mn}\,\phi_l$.

According to equation (19) this requires that

$$(K_l{}^m\, \alpha^n + \alpha^n\, K_l{}^m) + (K_l{}^n\, \alpha^m + \alpha^m\, K_l{}^n) = -\frac{8\pi ie}{hc}\, g^{mn}\,\phi_l \quad \ldots\ldots(23).$$

This means that the symmetrical part of $(K_l{}^m\,\alpha^n+\alpha^n\,K_l{}^m)$ is equal to

$$-(4\pi ie/hc)\,g^{mn}\,\phi_l.$$

If we write $l=m$ and sum over the values of m, we obtain as part of

$$(K_m{}^m\,\alpha^n+\alpha^n\,K_m{}^m)$$

the expression $-(4\pi ie/hc)\,\phi^n$, showing how ϕ^n is introduced into the theory through $K_m{}^m$ as required by equation (10).

The discussion has been concerned with the symmetrical parts of certain quantities entering the equations and we have omitted any reference to the antisymmetrical parts. These have not been determined by comparison with the quantum theory but we must examine whether any special conditions are required by the theory which in any way limit them.

§ 8. THE ANTISYMMETRIC PART OF $T_{mn}{}^l$

Let us suppose that the quantity $T_{mn}{}^l$ introduced in equation (4) consists of a part $S_{mn}{}^l$ symmetric in m, n and of $A_{mn}{}^l$ antisymmetric in these suffixes. The theory requires us to relate $T_{mn}{}^l$ with the electromagnetic potential in accordance with equations (19) and (23) and the relation enables us to modify Weyl's theory in accordance with equation (21). The circumstances are similar to those existing in Eddington's generalization of the theory of parallelism. $S_{mn}{}^l$, $A_{mn}{}^l$

If we make use of a relation introduced by him[5], the application of our theory can be easily understood although it may not be necessary to limit ourselves to the particular form employed. In the theory $\Gamma_{mn}{}^l$ is taken to be symmetric in m, n and thus differs from our case. Let us write

$$S_{mn}{}^l=a'\,(g_{mn}\,\phi^l-\delta_m{}^l\,\phi_n-\delta_n{}^l\,\phi_m),$$

where a' is a constant and is equal to $\pi ie/hc$ in the present application. If we form the expression $g^{rn}\,T_{rl}{}^m$, we now obtain a'

$$g^{rn}\,T_{rl}{}^m=a'\,(\delta_l{}^n\,\phi^m-\delta_l{}^m\,\phi^n-g^{nm}\,\phi_l)+g^{rn}\,A_{rl}{}^m \qquad \text{.....(24).}$$

The part of this symmetrical in m, n is

$\frac{1}{2}\,(g^{rn}\,T_{rl}{}^m+g^{rm}\,T_{rl}{}^n)$, equal to $-a'\,g^{nm}\,\phi_l+\frac{1}{2}\,(g^{rn}\,A_{rl}{}^m+g^{rm}\,A_{rl}{}^n)$ ...(25).

According to equation (23) this expression is equal to $-(2\pi ie/hc)\,g^{mn}\,\phi_l$ and thus with the above value of $S_{mn}{}^l$ we have to satisfy the further condition

$$g^{rn}\,A_{rl}{}^m+g^{rn}\,A_{rl}{}^n=-\frac{2\pi ie}{hc}\,g^{mn}\,\phi_l \qquad \text{.....(26).}$$

Let us turn to the effect of this upon equation (16), which contains

$$\Delta_{nm}{}^m=\Gamma_{nm}{}^m+T_{nm}{}^m=\Gamma_{nm}{}^m+S_{nm}{}^m+A_{nm}{}^m.$$

The value of $S_{nm}{}^m$ is $-(4\pi ie/hc)\,\phi_m$, as may be seen from the above value of $S_{mn}{}^l$. In order to obtain $A_{nm}{}^m$, multiply equation (26) by g_{pn} and write $m=l$, summing over the values of m.

We obtain

$$A_{pm}{}^m=-\frac{2\pi ie}{hc}\,\phi_p.$$

Thus equation (16) becomes

$$\frac{\partial \alpha^m}{\partial x^m} + \Gamma_{nm}{}^m \alpha^n = \frac{4\pi ie}{hc} \phi_n \alpha^n \qquad \ldots\ldots(27).$$

It is interesting to note that equation (19) is satisfied if $K_l{}^m$ contains an expression of the form $(\alpha^m \Gamma_l - \Gamma_l \alpha^m)$, where Γ_l is a matrix. The use of equation (15), in deriving equation (19) from which $\left(\frac{\partial \alpha^p}{\partial x^m} + \Gamma_{nm}{}^p \alpha^n\right)$ has vanished, thus suggests that this expression is of the above form and that we can write

$$\frac{\partial \alpha^p}{\partial x^m} + \Gamma_{nm}{}^p \alpha^n = \alpha^m \Gamma_l - \Gamma_l \alpha^m \qquad \ldots\ldots(28).$$

This particular relation is of great importance in Schroedinger's theory[6] of the generalized quantum equation.

§ 9. THE QUANTUM EQUATION AND THE ELECTROMAGNETIC THEORY

It is thus shown to be possible to develop a modification of the theory of electromagnetism proposed by Weyl as a consequence of the development of the quantum equation from the concept of the matrix length.

This indicates the existence of a close relation between the two branches of physics and provides us with a unitary theory embracing them. The theory includes also the relativity theory of gravitation, since the processes are those of general relativity. The modification of Weyl's theory coincides with that previously suggested and with that developed by London.

According to equation (20), l being used again as the scalar length,

$$\frac{\delta l}{l} = -\frac{2\pi ie}{hc} \phi_m \delta x^m,$$

corresponding to a scale factor $\exp\{(2\pi ie/hc) \int \phi_m \, dx^m\}$, for clearly this factor, multiplied by l, gives an invariant length.

This suggests that any function $F \exp\{(2\pi ie/hc) \int \phi_m \, dx^m\}$ may be used as a
F scale factor, where F is a function of the coordinates, and, from the occurrence of ψ as the scale factor in our theory, we naturally turn to that function to see if it is of this form. The square of the length is equal to

$$\alpha^m A_m \alpha^n A_n,$$

L so that the invariant length would be expected to be L, where

$$L^2 = \alpha^m \alpha^n A_m A_n \psi = l^2 \psi.$$

but this is a matrix with four components $l^2\psi_n$ and thus each component must satisfy the condition of invariance. Thus we have to examine whether ψ_n is of the correct structure.

If we turn to some of the problems treated we shall see that this is the case. Thus in the special case of an electron moving along the axis of x in an electrostatic field, we find that a solution is sought of the form $\psi = \psi_0 \exp\{(2\pi i/h)(px - Et)\}$,

where p is the momentum and E the energy. In this case, if the electrostatic potential is ϕ and we use the relativistic form, $E=(mc^2+e\phi)$. This solution is a particular case of the general form p, E

$$\psi=\psi_0 e^{\left(\frac{2\pi i}{h}\right)\int \Pi_n dx^n},$$

where Π_m is the generalized momentum introduced by Wilson and denotes $(p_m+ec^{-1}\phi_m)$. In the case considered $\Pi_4=iE/c$, and $\Pi_1=p$. It is clear that ψ is of the correct form, for it contains the required exponential factor. Π_m

But it is interesting to note that in this case we are neglecting any contribution to the change of length made by the factor

$$e^{\frac{2\pi i}{h}\int p_m dx^m}.$$

In other words we regard this quantity as if it were included in ψ_0 and, with it, had no influence on the metric. Since

$$p_m dx^m = m_0 g_{mn}\frac{dx^n}{d\tau}\frac{dx^m}{d\tau}d\tau$$

$$= -m_0 c^2 d\tau,$$

the expression becomes $e^{-\frac{2\pi i}{h}m_0 c^2 \tau}$.

For the sake of symmetry we write

$$c\tau = x^5, \quad \frac{e}{c}\phi_5 = -m_0 c,$$

so that the factor becomes $e^{\frac{2\pi i e}{hc}\int \phi_5 dx^5}$.

Thus if we had made use of a five-dimensional system the complete scale factor could have been written

$$e^{\frac{2\pi i e}{hc}\int \phi_\mu dx^\mu},$$

where the summation over μ is from 1 to 5.

In such a system of coordinates the fifth matrix α_0 would have been included in association with the fifth axis and would have appeared symmetrically with the other four.

It appears that the omission of $\exp(2\pi i/h)\int p_m dx^m$ is due to the use of only four coordinates and that this system allows something to escape from our scale factor. The use of the parallel displacement in association with the α^m restored the factor, but not with the same symmetry as that associated with a fifth coordinate.

The suggestion is that the scale factor should be used in the form given by

$$\psi_0 e^{\frac{2\pi i}{h}\int \Pi_n dx^m} = \psi_0 e^{-\frac{2\pi i}{h}m_0 c^2\tau + \frac{2\pi i e}{hc}\int \phi_m dx^m},$$

and that each part is to contribute to the change of the length l, i.e. of the ordinary length, according to the formula

$$\frac{\delta l}{l} = -\frac{2\pi i e}{hc}\phi_m \delta x^m + \frac{2\pi i}{h}m_0 c^2 d\tau. \qquad \text{.....(29).}$$

§ 10. ON THE INTERPRETATION OF THESE RESULTS

We regard the existence of a definite change in the length of a vector, when it undergoes a parallel displacement, as associated with the presence of an electromagnetic field. This makes the first part of the change as represented by the first term on the right-hand side of equation (29) a physically observed quantity, which we observe as the electromagnetic field. But our ordinary measurements in space-time do not seem to take account of the second term, at any rate as a change in δl. The question is how we can account for this fact, since the term itself has a place in the quantum equation and thus corresponds to a physical quantity. We suggest that it escapes us because in all physical measurements we observe only changes in δl corresponding to a complete period in x^5, i.e. our observations are on integral multiples of units of x^5 of magnitude h/m_0c. This being so $\exp\{(2\pi i/h)(mcx^5)\}$ always changes by unity and with reference to τ we can say that, in the observation of a particle, intervals of proper time less than h/m_0c^2 have no physical significance.

This principle of minimum proper time has been stated before[7] and is in agreement in principle with the view expressed by Ruark[8] that an element of absolute uncertainty exists in association with the location of a particle of magnitude h/mc. Many writers have made a similar suggestion and the fact that the conclusion is reached from many differing points of view seems to show that it is an expression of some physical law. It is interesting to note that in terms of ordinary space and time there is a lower limit to these elements respectively of $h\beta/m_0c\sqrt{(1-\beta^2)}$ and $h/m_0c^2\sqrt{(1-\beta^2)}$, where β is v/c. The meaning is that in the study of the track of a moving particle the accuracy of location is limited. When the velocity becomes very large the location is impossible and we cannot describe the motion as that of a particle, since some degree of location is associated with the concept of a particle. When v/c has the value $1/\sqrt{2}$ the value of the space limit is h/m_0c. Thus if we are studying the length of the track of a particle of this order of magnitude, the error is of the same order as the length itself when the ratio v/c becomes appreciable. Any conclusions drawn in such a case are therefore untrustworthy.

Some of these remarks have been made before, but the result has never been deduced in association with Dirac's equation. We have seen that it is closely associated with that equation, both being part of the same theory.

It seems clear that an element is missing from the quantum theory in its present form. The use of an exclusion principle and the occurrence of negative energy-states indicate the need of a new guiding principle as part of the theory. The derivation of the quantum equation and the interpretation of the change of length during a parallel displacement which has been given here are to be regarded as a search for a new feature. The principle of minimum proper time is itself of the nature of an exclusion principle, limiting the region of application of the quantum equation. The principle suggests that this equation must not be applied when the region is one where changes occur in a distance of h/m_0c; in fact, it suggests that to speak of changes of this kind in association with particles does not correspond to

physical reality, when applied to cases of very rapid motion. This being the case our development of the equation shows it to be part of a theory which sounds a note of warning when we approach the confines of its domain.

It is interesting to note that in connexion with discussions on the probability of transitions to states of negative energy, Bohr has expressed the opinion that finite probabilities are to be expected when a change of potential of the order m_0c^2 occurs in a distance of magnitude h/m_0c. This expression of opinion has been verified by a calculation by Sauter[9], who applied Dirac's equation to the problem.

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NOTE ON THE THREE ABSOLUTE SYSTEMS OF ELECTRICAL MEASUREMENTS

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In dealing with electrical and magnetic problems we have, in the most general case, to consider three systems of forces between the quantities concerned. These are (1) forces between quantities of electricity, (2) forces between quantities* of magnetism and (3) forces between electrical currents and quantities of magnetism.

Each of these sets of forces can be expressed in terms of the electrical and magnetic quantities concerned, but such expressions will be arbitrary, depending on the arbitrarily selected units, in terms of which the quantities dealt with are defined and measured.

If we wish to make the measures absolute, i.e. to express them in terms of the "absolute unit" of force, that force which produces unit acceleration in unit mass, we must multiply the arbitrary values by suitable coefficients and there will be three of these corresponding to the three classes of force just enumerated. These coefficients are generally denoted by the symbols k_0 μ_0, and A. They are all arbitrary but their selection will define the units in terms of which our electrical quantities must be measured if we wish the forces between them to be measured absolutely.

Now the theory of dimensions shows us that the dimensions of $A^2/k_0\mu_0$ are those of the square of a velocity, while it follows from electrical theory that the velocity is c, the velocity of wave propagation. Thus $A^2/k_0\mu_0 = c^2$. (It is perhaps important to note that in 1868, when the absolute theory was being developed, this was not known.) It follows, therefore, that of the three coefficients any two can be treated as arbitrary and independent, and the third is then fixed. Moreover, our equations expressing (1), (2), (3) will be simplified if as many as possible of the coefficients are arbitrarily made unity.

Maxwell accordingly chose to make A equal to unity. It was then open to him to make either μ_0 equal to 1, when we have the electromagnetic system, or k_0 equal to 1, the electrostatic system. But there is a third alternative—indeed many more are possible; we can make both μ_0 and k_0 equal to unity. Then we are left with $A^2 = c^2$ or $A = c$. This is Gauss's system. These are the three most simple systems ordinarily employed, and all are direct consequences of the result that in the endeavour to express electrical and magnetic forces in absolute measure we necessarily introduce two arbitrary coefficients, to each of which we assign the value unity, as leading to the simplest and most direct relations between electrical

* We are generally agreed that a quantity of magnetism "is only another term for a distribution of electrical currents", but as Maxwell showed, it is useful, and for the present necessary, in the theoretical and mathematical development of the subject to retain the idea of a magnetic pole.

quantities and the fundamental units of length, mass and time. Each of the systems has its own use. We cannot say that any other system replaces the three systems now in use, namely the absolute electrostatic c.g.s. system, the absolute electromagnetic system and the practical series.

The first two systems are closely connected. Thus on the electromagnetic system we have

$$f=\frac{mm'}{\mu_0 r^2}; \quad f=\frac{qq'}{k_0 r^2}; \quad f=\frac{mids\sin\phi}{Ar^2},$$

with $\mu_0=1$ and $A=1$.

But

$$A^2/\mu_0 k_0=c^2,$$

$$\frac{1}{k_0}=c^2,$$

$$f=\frac{qq'c^2}{r^2}=\frac{cq\times cq'}{r^2}=\frac{\epsilon\epsilon'}{r^2};$$

i.e. if $\epsilon=cq$, $\epsilon'=cq'$, i.e. if ϵ and ϵ' are quantities of electricity measured in terms of a unit quantity which is $1/c$ of that in which q and q' are measured, and in a medium in which μ_0 is unity (free space) the quantities q, q' repel each other with a force which is exactly the same as that between the quantities ϵ, ϵ' in a medium in which k_0 is unity (also free space) when electrostatic units are employed.

Just as in some cases it is preferable to measure mass in kilogrammes, in others in milligrammes, so in some cases it is useful to measure electricity in terms of a unit which in free space repels an equal unit with unit force, in others it is desirable to employ a unit of electricity such that the force will be c^2 units of force.

Electrotechnicians find this last unit more convenient, but this method even when expressed in terms of some new system of units cannot replace the other.

APPENDIX A*

INTENDED SUBSTITUTION OF THE PRACTICAL ABSOLUTE SYSTEM OF ELECTRICAL UNITS FOR THE EXISTING INTERNATIONAL SYSTEM

Statement issued by the International Committee

After a revision in 1921 of the international treaty known as the "Convention du Mètre", under which at present thirty-two nations co-operate in the maintenance of the international prototype standards of the metre and kilogramme,

* Appendix A is a translation from the original French text of a series of resolutions approved for publication by the International Committee of Weights and Measures in October 1935. Appendices B and C relate to the question of the choice of the fourth (electrical) unit. The International Electrotechnical Commission, having recommended the adoption of the m.k.s. system of electrical units, known as the "Giorgi system", referred the question of the fourth unit both to the International Committee of Weights and Measures and to the S.U.N. Committee of the International Union of Physics for advice. Appendix B is a translation of resolutions dealing with this question approved by the International Committee of Weights and Measures for transmission to the I.E.C., and Appendix C is the reply of the S.U.N. Committee to the I.E.C. The three appendices together indicate the present position with regard to the intended eventual establishment of the system of practical electrical units on a self-consistent absolute basis.

authority was entrusted by the Conférence Générale des Poids et Mesures to the Comité International des Poids et Mesures in 1927 to take up also the question of electrical units. An advisory electrical committee, including representatives of the principal national laboratories, was appointed, and acting on the advice of this committee, the International Committee in 1933 recommended, and the Conférence Générale of that year approved in principle, the eventual substitution of the practical absolute system of electrical units for the present international system. The Conférence further instructed the Comité International to take the necessary steps to give effect to this decision.

At its meeting in October 1935 the Committee decided that the work on the subject which has been in progress for so many years in the various national laboratories had reached a stage at which it was possible to fix a date for the change, and authorized the publication of the following statement (translated from the original French text):

"1. In accordance with the authority and responsibility placed upon it by the General Conference of Weights and Measures in 1933, the International Committee of Weights and Measures has decided that the actual substitution of the absolute system of electrical units for the international system shall take place on the 1st January, 1940.

"2. In collaboration with the national physical laboratories, the Committee is actively engaged in establishing the ratios between the international units and the corresponding practical absolute units.

"3. The Committee directs attention to the fact that it is not at all necessary for any existing electrical standard to be altered or modified with a view to making its actual value conform with the new units. For the majority of engineering applications the old values of the international standards will be sufficiently close to the new for no change, even of a numerical nature, to be required. If for any special reason a higher precision is necessary numerical corrections can always be applied.

"4. The following table gives a provisional list of the ratios of the international units to the corresponding practical absolute units, taken to the fourth decimal place. Since differences affecting the fifth decimal place exist between the standards of the international units held by the various national laboratories and also because all the laboratories which have undertaken determinations of the values of their standards in absolute measure have not yet obtained final results, the Committee does not consider it desirable for the present to seek a higher precision. At the same

Table

1 ampere	international	= 0·999 9	ampere	absolute
1 coulomb	,,	= 0·999 9	coulomb	,,
1 ohm	,,	= 1·000 5	ohm	,,
1 volt	,,	= 1·000 4	volt	,,
1 henry	,,	= 1·000 5	henry	,,
1 farad	,,	= 0·999 5	farad	,,
1 weber	,,	= 1·000 4	weber	,,
1 watt	,,	= 1·000 3	watt	,,

time it hopes that it will be possible to extend the table of these ratios with a close approximation to the fifth decimal place well before the date fixed for the actual substitution of the practical absolute system for the international system."

APPENDIX B

RESOLUTIONS*, RELATIVE TO THE CHOICE OF A FOURTH UNIT IN THE GIORGI SYSTEM, ADOPTED BY THE COMITÉ CONSULTATIF D'ÉLECTRICITÉ AT ITS MEETING IN SEPTEMBER 1935 AND APPROVED BY THE COMITÉ INTERNATIONALE DES POIDS ET MESURES

Resolution 5*a*, after a statement as to the dependence of the Comité Consultatif on the International Committee, continues:

"The Comité Consultatif considers that in the first place it should draw attention to the fact that an important majority among the members present expressed the opinion that the connexion between mechanical and electrical units should be secured by assigning the value 10^{-7} in a non-rationalized m.k.s. system, or $4\pi.10^{-7}$ in a rationalized system, to the quantity which is generally known as the 'permeability of space'.

"On attention being called to the fact that the form in which the question was put limited the choice to the seven practical units (coulomb, ampere, volt, ohm, henry, farad and weber), the Committee unanimously agreed that the only choice lay between the ampere, defined as being one-tenth of the c.g.s. electromagnetic unit of current, and the ohm, defined as 10^9 times the electromagnetic unit of resistance, these two quantities being consistent with the values 10^{-7} and $4\pi \times 10^{-7}$ indicated above for the permeability of space.

"Finally the Committee decided in favour of the ohm by the narrow majority of 4 votes against 3 for the ampere; one member did not vote."

Resolution 5*b*. This refers to a note presented by Mr Sears at the following Session of the Comité Consultatif which, it is recorded, "received the unanimous and favourable approval of the Comité who decided to transmit it (as part of their report) to the International Committee" by which it was subsequently approved, subject to possible small changes in detail. The text of the note is as follows:

"1. Electromagnetic theory leads to the relation $A^2 = \mu_0 k_0 c^2$ between the four quantities represented in the formula. Of these c is the velocity of propagation of electromagnetic waves in space; μ_0 the magnetic permeability of space; k_0 the inductive capacity of space (permittivity); and A a constant coefficient. To obtain a complete theoretical system of electrical units, the values of two of the three quantities A, μ_0 and k_0, must be fixed independently. The third is then also fixed by the relation quoted above.

"2. The magnitudes of the electrical units of the system, the adoption of which

* Translated from the *Report* made by the Comité Consultatif to the International Committee of Weights and Measures.

was sanctioned by the Conférence Générale of 1933, are identical with those of the practical units derived from the classical c.g.s. system of Maxwell.

"3. These systems are based essentially on the conception of a constant value for the permeability of space, this value in Maxwell's system being numerically equal to 1. For the m.k.s. system, not rationalized, this permeability should have the value 10^{-7}, and for the m.k.s. system, rationalized, the value $4\pi.10^{-7}$. In each of these systems the coefficient A is taken as a numerical constant to which the value unity is assigned. Thus it does not appear again in the equations. The principal units of these two m.k.s. systems will then be the same as those of the practical system, the adoption of which has been sanctioned by the Conférence Générale of 1933.

"4. The various electrical units can all be derived from these conceptions by means of equations representing physical laws, and employing constants suitably selected. In principle no one of these units has priority over the others.

"5. The definitions adopted for the principal electromagnetic units might run as follows. (*a*) *Ampere*. The ampere is the constant current which, if maintained in two straight parallel conductors of infinite length at a distance of one metre apart in empty space, produces between these conductors a force equal to 2×10^{-7} m.k.s. units of force per metre length. (*b*) *Coulomb*. The coulomb is the quantity of electricity transported per second by a current of one ampere. (*c*) *Volt*. The volt is the difference of electrical potential between two points on a conducting filament carrying a constant current of one ampere when the power dissipated between these points is equal to the m.k.s. unit of power (watt). (*d*) *Ohm*. The ohm is the electrical resistance between two points of a conductor when a constant difference of potential of one volt applied between these points produces a current of one ampere in the conductor, provided that the conductor is not the seat of any electromotive force. (*e*) *Weber*. The weber is the magnetic flux which, when linked with a circuit of a single complete turn, would produce in that circuit an electromotive force of one volt if reduced to zero in one second at a uniform rate. (*f*) *Henry*. The henry is the inductance of a closed circuit in which an electromotive force of one volt is produced when the electric current in the circuit changes uniformly at the rate of one ampere per second. (*g*) *Farad*. The farad is the electric capacity of a condenser between the plates of which an electromotive force of one volt is produced when it is charged with one coulomb.

"6. These units may be derived as follows:

Ampere	I	: ampere	I
coulomb	Q	: ampere-second	IT
volt	E	: watt per ampere	PI^{-1}
ohm	R	: volt per ampere	EI^{-1}
weber	Φ	: volt-second	ET
henry	L	: volt-second per ampere	ETI^{-1}
farad	C	: ampere-second per volt	$E^{-1}TI$

"7. For the current practice of laboratory measurements at least two primary reference standards are necessary and should be suitably chosen from among the

various units. The two reference standards should be the ohm and the volt of which the former is realized in the form of resistance coils; the latter in the form of Weston cells.

"8. For theoretical questions, such as the dimensional equations connecting the various units, the most convenient unit as a starting point for the derivation of the whole system of electromagnetic units appears to be the ampere, which is linked directly by simple relations both with the fundamental basis of the system and also with the other electric and magnetic quantities and which, moreover, has the advantage of eliminating fractional powers in the dimensional equations. From this point of view the ampere should be preferred as the fourth unit necessary to complete the m.k.s. system of electromagnetic units."

APPENDIX C

THE M.K.S. SYSTEM OF ELECTRICAL UNITS*

Reply from the S.U.N. Commission† of the International Union of Pure and Applied Physics to the request for advice on the choice of the fourth unit of the Giorgi system of units, contained in a letter dated June 27, 1935, to Prof. Abraham, Secretary of the International Union from Prof. Kennelly, Chairman of the E.M.M.U. Committee of the I.E.C.

The S.U.N. Commission has given very careful consideration to the request of the I.E.C. for help in the selection of the fourth quantity which, in the view of the I.E.C., is required to complete the m.k.s. system of units and desire to thank the I.E.C. for referring the question to the Commission.

The table which accompanies this reply has been prepared to show the relation between some of the quantities concerned in the m.k.s. and c.g.s. systems respectively.

The Commission has consulted a large number of leading physicists and, with hardly any exception, the following resolution, proposed by Dr Abraham, Secretary of the International Union of Pure and Applied Physics, has been approved.

"Considérant que lors de leur création les unités électromagnétiques du système pratique avaient été définies comme étant des multiples décimaux exacts des unités électromagnétiques c.g.s.

"Considérant que ces définitions initiales comportent plus de précision expérimentale et plus de securité que des définitions basées soit sur la conservation de certains étalons soit sur des techniques spéciales (colonnes de mercure, électrolyse).

* In the *Report* of the S.U.N. Commission approved by the International Union in October 1934 the value of B/H is given as μ_0, not μ_0/A. The difference is due to the fact that in that proof it was assumed that $A=1$. If the symbol A is retained, the potential energy of a pole is miw/A and thus we obtain $B/H=\mu_0/A$.

† Sir Richard Glazebrook, President; Prof. Abraham (France); Prof. Kennelly (U.S.A.); Prof. Fabry (France); Prof. Keesom (Holland); Dr Ezer Griffiths, Secretary.

"La Commission émet l'avis;

"Il n'y a pas lieu de modifier les définitions initales des unités électriques du système pratique, définitions qui fixent pour ces unités des valeurs égales à des multiples décimaux exacts des unités du système c.g.s. électromagnétique."

The Commission are pleased to learn from a letter* from Prof. Marchant that at the I.E.C. meeting, although there is nothing in the minutes stating that the basis of the decision should be that the permeability of free space should be taken as unity, the reason why the question of the fourth unit was referred to the two Committees concerned was that the Commission was anxious that whatever was chosen should be consistent with the c.g.s. system of units. The table gives effect to this view. The S.U.N. Commission therefore recommend *that the table appended to this Report be accepted generally as defining the relation between the c.g.s. and the m.k.s. system of units.*

The accepted system of electrical measurements is based on the *Reports* of the British Association Committees on Standards for Electrical Measurements, 1861–70, 1880–1912. The Committee in 1863 decided to employ the absolute system of measurement which they explained in the following terms (p. 112):

"'The word 'absolute' in the present sense is used as opposed to the word 'relative' and by no means implies that the measurement is accurately made or that the unit employed is of perfect construction; in other words it does not mean that the measurements or units are absolutely correct but only that the measurement, instead of being a simple comparison with an arbitrary quantity of the same kind as that measured, is made by reference to certain fundamental units of another kind treated as postulates."

The fundamental units selected were those of length, mass and time. For the construction of standards of measurement the knowledge is required of the forces between electrical and magnetic quantities expressed in these fundamental units. Theory shows that, under the conditions assumed by Maxwell, one additional quantity is necessary, and is sufficient, to give us that knowledge. Theory also shows that this quantity, usually denoted by the symbol μ_0, is a measure of the permeability, that is the ratio of magnetic induction to magnetizing force, in free space, the medium in which the measurements are supposed to be made. On the c.g.s. system the value of μ_0 is assumed to be unity. The m.k.s. system can be made absolute by the assumption of any convenient value for μ_0, but if the units of that system are to be the practical units of the c.g.s. system the value† of μ_0 must be 10^{-7}.

In reply therefore to the request from the I.E.C. the S.U.N. Commission recommend *that the fourth unit on the m.k.s. system be* 10^{-7} *henry per metre, the value† assigned on that system to the permeability of space.*

* *Nature*, Lond., p. 110 (July 20th, 1935).

† On the rationalized system of units the value will be $4\pi \times 10^{-7}$.

Table showing the relation between quantities on the c.g.s. electromagnetic system and on the proposed m.k.s. system

	Length	Mass	Time	Magnetic coefficient μ_0	Electro-magnetic coeffi-cient A	Space permea-bility μ_0/A	Cou-lomb	Ampere	Volt	Ohm
c.g.s.	1 cm.	1 gramme	1 second	1	1	1	10^{-1}	10^{-1}	10^{8}	10^{8}
m.k.s.	1 metre	1 kilogramme	1 second	10^{-7}	1	10^{-7}	1	1	1	1

On a modern Maxwell theory of electricity the permeability of space, which is measured by the ratio μ_0/A, is assumed to be a quantity having dimensions. Its value, therefore, will depend on the system of units employed. On the c.g.s. system the permeability of space has been selected as the unit of permeability. Hence on this system, since $A=1$, the value of μ_0 is unity. On the m.k.s. system the value of μ_0 is 10^{-7}, and on the rationalized m.k.s. system it is $4\pi \times 10^{-7}$.

At the same time the S.U.N. Commission desire to take this opportunity of placing on record their recognition of the fact that there are important electrical theories supported by a number of physicists in accordance with which $A=c$, the velocity of wave propagation, and $\mu_0 k_0$ is a pure number.

537·71

THE FOURTH UNIT OF THE GIORGI SYSTEM OF ELECTRICAL UNITS

By The Late Sir R. T. GLAZEBROOK, F.R.S.

Received December 6, 1935. *Read in title March* 6, 1936

In a recent letter from Berlin, a valued correspondent, to whom I am indebted for much assistance in connexion with electrical units, sent me the following series of equations to show that "if in addition to the mechanical quantities one takes a single electrical quantity, for preference a quantity of electricity Q, it is possible to deduce all electrical quantities from this by means of a series of equations in each of which one and only one new electrical quantity appears". The question is discussed* more fully in Geiger and Scheel's *Handbuch der Physik*.

Equation	Quantity defined
$f=EQ$	E (field-strength)
$V=\int Edl$	V (voltage)
$Q=\int DdS$	D (displacement)
$I=dQ/dt$	I (current)
$f=I\,(lB)$	B (induction)
$\int Hdl=I$	H (field-strength)
$dI=kEdS$	k (conductivity)
$E=\frac{1}{K}D$	K (dielectric constant)
$B=\mu H$	μ (permeability)
$f=mH$	m (pole-strength)

My correspondent in a later letter emphasizes the fact that this is only given as an example. One might, he says, start from the equation $f=mH$ assuming m as the fourth unknown. In my reply I have expressed my general agreement with this as the basis of a mathematical theory of electricity and have suggested that in our correspondence we have had in view two different aspects of the matter. It is the purpose of this paper to explain the difference.

It was not the object of the British Association Committee in 1863 to establish the mathematical theory of electricity. Maxwell had that in view later when writing his book, and the equations quoted above are all, I think, to be found in that book. The existence of quantities of electricity, electric currents, etc., is assumed in such a theory, but this was not the raison d'être of the B.A. Committee in 1863. Its full title is the "Committee of the British Association for improving the construction of Practical Standards for Electrical Measurements". To do this it was necessary to have clear ideas as to the theory on which those measurements were

* Geiger and Scheel, *Handbuch der Physik*, **11**, 10.

based, and the views of the Committee are set out by Maxwell and Fleeming Jenkin in Appendix C to the 1863 *Report*.*

It was the task of Maxwell and the B.A. Committee to develop a system which would enable them to construct apparatus—galvanometers, electrometers, ammeters and voltmeters we now call them—and resistance coils etc., for the determination of electrical quantities in absolute measure. The term "absolute measure" is explained in the *Report*. For this purpose the assumption of a fourth unit of the same fundamental nature as the units of length, mass and time, is not required and is misleading.

The series of equations given above, all of which are of course quite true, will not of itself enable us to construct a resistance coil or to set up apparatus for measuring currents and potentials. In the list f is the force (measured in terms of some definite unit of force, e.g. dynes) on a particle, a small sphere, carrying a quantity Q of electricity.

We can imagine this placed in a field of electrical force which is kept constant in time but varies from point to point of space. If we had the means of varying Q in a known manner and at the same time of measuring f at any given point of space we should find no doubt that the ratio f/Q remained constant and gave us the value of a quantity E which we denote as the electrical field-strength. By doing this at all points of space we could plot the field of force.

We come now to the second equation $V=\int E.dl$. Before this is of any practical use to us we must know the relation between E and l, and we must be able to express both in terms of the coordinates of the point at which E is measured and integrate the result. To do this with any hope of success it is necessary to simplify the conditions. Suppose that the electrical charges are all measured in terms of Q_0 the fourth unit of the system; any charges may then be expressed as MQ_0, NQ_0 etc., M, N etc. being numerics. If the field be due to a single charge MQ_0 concentrated at a point A we shall find of course that the force at a second point B is proportional to MQ_0, and by varying the charge NQ_0 at the point B at which the force f is measured we can prove that the force is proportional to MNQ_0^2, while by varying the distance r between the points A and B we can show that the force f dynes varies as MNQ_0^2/r^2. Thus we may write

$$f=\frac{MNQ_0^2}{kr^2},$$

where k is a constant required to express as dynes the force MNQ_0^2/r^2 which is given in some arbitrary units.

Let us now suppose that the experiments have been conducted in a vacuum and that we can repeat them in some other insulating medium; we shall obtain a similar result but with a different value for the constant k. Thus k is a function of the properties of the medium in which the measurements are made and may be denoted as k_0, k_1 etc. depending on the medium. But what we have done is simply to repeat Coulomb's experiments as extended by Faraday.

* Collected Volume of B.A. Electrical Standards *Reports*, p. 86.

Returning now to the vacuum we have

$$f_0 \text{ dynes} = \frac{MNQ_0^2}{k_0 r^2}.$$

Take the case in which M and N are each unity and r is 1 cm.—the assumed unit of length; then

$$f_0 = \frac{Q_0^2}{k_0}.$$

If further we prescribe that f_0 is to be 1 dyne, then

$$Q_0^2/k_0 = 1.$$

This equation can be satisfied by putting Q_0 and k_0 each equal to unity, i.e. by taking as our unit quantity of electricity that quantity of electricity which, in a field in which k_0 is unity, repels an equal quantity at a distance of 1 cm. with a force of 1 dyne. This, with the further assumption that k_0 is unity in a vacuum, is the definition of the electrostatic unit of electricity. The assumption that there actually exists a concrete fourth unit Q_0 which has this property is not necessary for our purpose. We may of course define Q_0 as the quantity which in a medium in which k_0 is unity repels an equal quantity at a distance of Q_0 centimetres with a force of 1 dyne, but we make no progress without some assumption as to the value of k_0, the link which transforms into dynes the arbitrary units in which the force MNQ_0^2/r^2 is measured, and when that assumption is made it is superfluous to treat Q_0 as a fourth fundamental unit *of the same kind* as those of length, mass and time.

So far we have only considered an electrostatic problem. We may deal in a similar manner with the two equations $f = mH$ and $\int Hdl = I$. I is known from the equation $I = dQ/dt$, but unless we can express H and dl as functions of the co-ordinates of the point at which H and dl are measured we cannot proceed, and we find that, as above, we must introduce a quantity μ_0, a function of the properties of the medium, in order to link up the unit of force, the dyne, with the arbitrary units in which m and H are measured. A third such link is required when we are dealing with the interaction between currents and magnetism involved in the equation*

$$f = I\,[lB].$$

This is usually denoted by the symbol A, and between the three we have the well-known relation $A^2/\mu_0 k_0 = c^2$, where c is the velocity of wave-propagation. The links are thereby reduced to two, A and μ_0 say. We cannot prescribe standards of measurement without assumptions as to these two quantities, and when these assumptions are made a fourth unit is not necessary for our purpose.

It is of course quite true that electrical theory assumes the existence of quantities of electricity, currents, magnets etc., and that the dimensional equations are simplified if expressed in terms of a quantity of electricity additional to those of length, mass and time, but the simplification of the dimensional equations was not the object of the B.A. Committee.

They set out to establish a set of standards for electrical measurements dependent

* The symbol [ ] indicates vector multiplication.

only on the three fundamental mechanical units, and by selecting as these fundamental units the centimetre, the gramme and the second, and assuming that in a vacuum the values of the two links A and μ_0 were each unity, they were able to do this and give us the c.g.s. system of practical units.

The same end is reached on the m.k.s. system if we assume for A and μ_0 the values 1 and 10^{-7} or on the m.k.s. rationalized system the values 1 and $4\pi.10^{-7}$. This is recognized by my correspondent, who, in his second letter to me, writes: "The Giorgi system is completely defined in the following statement: (1) the standards are M, K, S, μ_0. (2) Three of its units agree fully with the standards M, K, S, a fourth unit is $10^7\mu_0/4\pi$); all other units can be derived from these by the principle of coherence. (3) If for any special case it is desired or is necessary to select four fundamental units from these, every man may make his choice according to his own preference."

If to this is added the statement that it has been assumed throughout that the value of A is unity and that therefore $\mu_0 k_0 c^2 = 1$ I agree entirely, but I prefer to consider μ_0 as a link and not a fundamental unit. I also agree that the discussion as to the value of A is a matter for electrical theory to consider, not for standardization.

It is perhaps of interest in conclusion to develop the consequences of a haphazard choice of four fundamental units.

Let us assume we take as these E, volts or electromotive force, P, power, T, time, and m quantity of magnetism. These are independent; we might equally well choose $\overline{m}$ magnetic moment for m. Let L, M, F, W be dependent units of length, mass, force, and energy. By writing down the dimensional equations connecting these units with the four fundamental units—for instance $W = PT$, $F = W/L$—we can proceed to find the dimensions of the other electrical and magnetic quantities including μ and k.

But this will not enable us to construct standards. To do this we must know the value we assign to μ and also, if electrostatic quantities are to be included, to k. We must distinguish between methods of measurements, *Messtechnik* in my correspondent's words, and the mathematical theory of electricity.

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THE PROPERTIES OF HEUSLER'S ALLOY, AND THE TRUE SPECIFIC HEAT OF MANGANESE AND ITS DISCONTINUITY

By J. R. ASHWORTH, D.Sc.

Received September 19, 1935. *Read in title February* 7, 1936

ABSTRACT. The physical properties of a sample of Heusler's alloy made in Prof. F. C. Thompson's laboratory at the University of Manchester have been examined. The experiments, which were always carried out on the same specimen, comprised determinations of density, intensity of magnetization, critical temperature, Curie's constant, electrical resistivity and its temperature coefficient, thermoelectric power and mean and true specific heat. A determination has also been made of the true specific heat of the metal manganese and a large discontinuity has been found about 350° C., which is near to the critical temperature of Heusler's alloy. It was further found that the heat-capacity of the alloy is the sum of the heat-capacities of its constituents both below and above the critical temperature, thus following Regnault's rule, and the same rule can be applied to magnetite.

§ 1. INTRODUCTION

FERROMAGNETIC substances are so few in number that the discovery of Heusler's alloy made a welcome addition to the list. The fact that an alloy of manganese, aluminium and copper, metals which separately are non-magnetic, should be strongly magnetic is so remarkable that it makes the properties of this alloy well worth investigating.

Considerations of this kind prompted the initiation of a research on the magnetic, electric and thermal properties of the alloy, but since the research was begun a few years ago some experimental work on one or two divisions of the subject has been published by other investigators. Nevertheless what is now submitted not only serves as additional evidence for the conclusion of others but also supplies some information not comprised in their researches.

The results which are here given have, moreover, a unique feature inasmuch as they have all been derived from experiments on one sample of the alloy, and this removes any objection to the effect that the physical qualities which have been measured are not comparable on account of differences in the percentage composition or treatment of the alloy. It will not be necessary to refer at length to experimental details but the methods adopted and the results obtained are given in full.

The alloy upon which experiments have been made was kindly supplied by

Prof. F. C. Thompson and was made in his metallurgical laboratory at the University of Manchester. Its percentage composition is very approximately as follows:

Copper	... ...	59·2
Aluminium	... ...	17·6
Manganese	... ...	23·3
		100·1

These are nearly atomic proportions. In form it was a short stout rod, and there were also some fragments of irregular shape. The material as received was brittle and the rod accidentally falling on the floor broke into two pieces. These pieces were from 6 to 7 cm. in length and 1·32 cm. in diameter and weighed from 60 to 70 g. each.

The density, determined by two methods, was found to be 6·60 g./cm.^{3}, but at the conclusion of a long series of experiments in which the alloy had been repeatedly heated to a temperature as high as and above the critical temperature, it appeared to have become a little less and then stood at 6·56.

The properties of this alloy which have been examined are (i) the intensity of magnetization at saturation; (ii) the critical temperature; (iii) Curie's constant; (iv) the electrical resistivity and its temperature coefficient; (v) the thermoelectric power, more particularly in the vicinity of the critical temperature; (vi) the specific heat at air-temperature and at the critical temperature, and the discontinuity at the critical temperature.

§ 2. INTENSITY *I* OF MAGNETIZATION

I

One of the fundamental magnetic quantities to be determined and one of chief interest is the maximum intensity of magnetization. As the specimen was, in shape, a short stout rod the isthmus method described by Ewing was the most suitable and the one adopted for this determination.

The short rod was wound with a primary and two secondary coils and was closely fitted between the poles of a powerful electromagnet excited by a current of from 6 to 7 amperes, which was sufficient to magnetize the specimen to saturation. The induction was measured by suddenly withdrawing the alloy from the pole pieces and observing the consequent throw of the moving system of a ballistic galvanometer which had been carefully calibrated with a standard primary and secondary. The calculation of the induction requires a correction for the residual magnetism of the specimen, which however was small as the dimension ratio was small. An independent experiment was made which allowed the necessary correction to be made amounting to 121 lines per cm.^{2} The maximum induction was then found to be 5412 lines per cm.^{2} and the field 302 gauss, and from these facts it follows that the maximum intensity I_0 of magnetization, treated as magnetic moment per unit volume, is 416. It may also be calculated that the permeability at this high induction is a little more than 18 and the susceptibility 1·4.

I_0

A further experiment by a magnetometric method, whilst confirming the amount of the residual magnetism, at the same time allowed the critical temperature to be

determined. The alloy was heated gradually up to and beyond the critical point and readings were taken of the magnetometer. These showed but little change until near the temperature of 345° C., but above this point a rapid loss of magnetism occurred which became nearly complete about 375° C. The point where the loss of magnetism was most rapid was 360° and this may be taken as the critical temperature. Several other experiments to be described later confirm this temperature as a critical one.

The alloy on cooling remained virtually non-magnetic down to 350° C. and then slowly acquired magnetism. There was evidence of large hysteresis with temperature which perhaps was due in part to the small dimension-ratio of the specimen, but this question was not examined further.

θ

§ 3. THE CRITICAL TEMPERATURE θ

There are marked changes in other than magnetic properties which are generally found to take place in ferromagnetics near the critical temperature for magnetism, and it is probable that the temperature at which these changes take place is nearly the same for all. In no case are the changes absolutely abrupt, but the temperature at which they take place most rapidly may be considered to be the critical point in a critical region. We may group here the critical points from a consideration of several properties which exhibit distinctive changes at the magnetic critical temperature.

(*a*) The direct determination of the critical temperature for magnetism has already been mentioned and this temperature was estimated to be 360° C. (*b*) The temperature coefficient of electrical resistivity, as with iron and nickel, increases to a critical value and thereafter approximates to the normal rate. Experiments carried out on Heusler's alloy show that the critical point lies near to 356° C., a temperature rather lower than what has been found above. (*c*) When a thermo-junction of the alloy is heated, the regular progression of the thermoelectric power begins to change into a new direction at about 345° C. continuing to 385° C., and the change is most rapid about 362°, after which at temperatures higher than 385° it resumes a more normal course. The rapid change at 360° may be regarded as a critical temperature. (*d*) The alloy exhibits the rapid increase of true specific heat with rise of temperature and abrupt fall at the critical temperature which is characteristic of ferromagnetics, and experiments show that a maximum true specific heat and discontinuity occur very close to 364°.

Collecting these results together we have for the critical temperature: From magnetic experiments (*a*) 360°, from electrical resistivity (*b*) 356°, from thermo-electric power (*c*) 360°, from specific heat (*d*) 364°. The mean of these is very nearly 360° C.

§ 4. CURIE'S CONSTANT

The difficulties of determining Curie's constant are very much reduced if a comparative method is employed. A preliminary theoretical examination showed that this constant would probably be of the same order as for nickel and so it was

decided to make a comparison with nickel, more especially as Curie's constant for nickel has been determined with considerable precision and is perhaps better known than that for any other ferromagnetic.

The apparatus was in all essential points a copy of the torsion balance devised and used by Pierre Curie. The torsion wire was of silver 0·2 mm. in diameter and was attached to a torsion head divided into 100 divisions. The lower end of the wire carried an arm to one end of which was fixed the carriage for the metal to be tested, the other end of the arm being weighted with a counterpoise. The holder for the specimen was a small thin-walled glass tube. To ascertain when the arm was brought to the fiducial position a pencil of light was projected on to a mirror fixed to the vertical axis of the moving system, and the reflected ray fell on a scale at a distance of a metre from the mirror.

The heating-coil, which was wound non-inductively and supplied with an alternating current, was fixed firmly between the poles of a strong electromagnet which was maintained at constant excitation. Lastly the temperature of the specimen was determined from the readings given by a thermocouple of platinum and platinum-iridium on a scale one metre from the galvanometer. The disposition of heating-coil, holder, thermojunction and electromagnet was in general as in Curie's well-known experiments[1].

Weighed fragments of nickel and of Heusler's alloy were tested in alternate series of experiments and values proportional to the product of the susceptibility and excess of temperature above the critical temperature were obtained for each metal.

If C_n and C_a are Curie's constant for nickel and the alloy and K_n and K_a the mass susceptibilities respectively at any temperature T, above the critical temperature θ, we have

$$\frac{C_a}{C_n} = \frac{K_a(T-\theta_a)}{K_n(T-\theta_n)}.$$

A number of concordant determinations gave the ratio of C_a to C_n as 152·0 to 184·5 for equal masses, which is equal to 0·824.

Weiss and Foëx[2] found the Curie constant for nickel in mass units to be 0·00540; hence Curie's constant for Heusler's alloy is 0·00540 × 0·824 or 0·00445. If the density of the alloy is 6·60 the constant in volume units (cm³) is 0·0294. The reciprocal R' of Curie's constant for Heusler's alloy is therefore 34·1. A small correction to this number may be made to allow for a slight paramagnetism of the glass holder, and the final result is 34·0.

§ 5. ELECTRICAL RESISTIVITY AND ITS TEMPERATURE COEFFICIENT

For the determination of the electrical resistivity of the alloy a fall of potential method was employed. The alloy was in the form of a stout rod and a current of about 4 amperes was passed through it, whilst the fall of potential between two points was compared with that across a standardized resistance in circuit with the

alloy. Arrangements were made for the reversal of the current and pairs of readings were taken for different currents.

Observations taken in this way led to the value $83 \times 10^{-6}\ \Omega$. for the resistance between the two specified points 5·4 cm. apart. The sectional area of the alloy being 1·327 cm^2, the resistivity is thus found to be $20{\cdot}4 \times 10^{-6}$, that is, 20·4 microhms per centimetre cube at air temperature.

The variation of resistivity with temperature was next determined, and now the only change required was to embed the alloy in a sand bath which could be evenly heated by a row of Bunsen flames. A thermometer graduated to 410° C. in contact

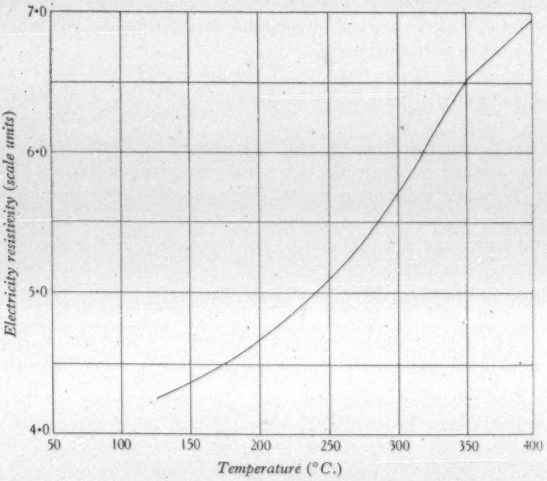

Figure 1. Electricity resistivity of Heusler's alloy.

with the alloy gave readings of the temperature which was slowly raised to 395° and as slowly lowered to the temperature of the room. The usual precautions were taken to eliminate thermo-currents and errors due to want of symmetry of the apparatus. The accompanying graph, figure 1, exhibits the results. When the alloy was heated the resistance increased, at an increasing rate, to between 350° and 360° C. at which point the rate of change became slower, and thereafter the increase of resistance was at a nearly constant but slower rate than at temperatures just below 350°. It is about 360° C. that the change per degree was most pronounced and this corresponds with the temperature at which magnetism is being most rapidly lost.

The temperature coefficient between 25 and 125° is 0·0016, which is comparable with other alloys but much less than for pure metals and very much less than for the pure magnetic metals.

O. Heusler's experiments[3] on five samples of the alloy with different percentages of manganese, copper and aluminium show great variations in electric resistivity. They range from $76{\cdot}2\times10^{-6}$ to $15{\cdot}8\times10^{-6}$ at 20° C., and the temperature coefficients at these extremes, referred to 20° C., are 0·00166 and 0·00207 respectively.

A recent valuable research by Y. Matuyama[4] on the magneto-resistance of magnetic metals for longitudinal magnetic fields at low and high temperatures includes among these metals Heusler's alloy and traces at the same time the curve of its resistivity and temperature. The alloy contained 70·39 per cent of copper, 12·27 per cent of aluminium and 17·34 per cent of manganese. The temperature coefficient of resistance between 0° and 100° was 0·00166, which agrees with the specimens of the alloy cited above; the rate of change of resistance increased rapidly towards 300° C. and thereafter became much less. Thus 300° C. appears to be the critical temperature.

It is shown that the negative value of the magneto-resistance, $\Delta R/R$, always increases with field strength in a longitudinal magnetic field, and the absolute value of $\Delta R/R$ is very large at low temperatures, but it decreases rapidly with rise of temperature and becomes zero from 290 to 330° C. Magneto-resistance is therefore a property characteristic of the ferromagnetism of the alloy and vanishes with its loss. Iron, nickel and cobalt are found to exhibit a similar behaviour in this respect, the magneto-resistance vanishing or becoming exceedingly small at the critical temperature.

§6. THERMOELECTRIC POWER

The thermoelectric power of iron and nickel shows a decided change in the neighbourhood of the critical temperature, a rapid augmentation taking place from less to greater positive values in iron and from greater to less negative values in nickel. It is therefore of interest to determine the behaviour of Heusler's alloy when it forms one of the metals of a thermoelectric couple. A junction of German silver and the alloy gave a suitably large e.m.f. on being heated and arrangements were made to work with this pair of metals.

The rod of Heusler's alloy was fixed with one end projecting into a lead box filled with cold water, which was kept flowing through the box at a rate which maintained the temperature constant; the other end of the rod in contact with the German silver was inserted in a hard glass tube on which a coil of high resistance wire was wound, the whole being jacketed with asbestos. The free end of the German silver wire was carried to a high-resistance galvanometer and the circuit was completed by connecting the second terminal of the galvanometer to the end of the alloy in the cold water.

Readings of the temperature of the hot junction were made by means of a nitrogen-filled mercurial thermometer graduated to 410° C., but in some later experiments a platinum and platinum-iridium thermojunction was used. The various connexions throughout the circuit were carefully protected from accidental changes of temperature.

By gradually increasing the strength of the current through the heating spiral the hot junction was submitted to a slow uniform rise of temperature whilst the cold junction was steadily maintained at the temperature of the cold water. Preliminary experiments showed that some change in the regular rise of the thermo-

Table 1. Thermoelectric power of Heusler's alloy against German silver

Temperature (°C.)	Thermo-e.m.f. (μV.)	Thermo-electric power (μV./°C.)	Temperature (°C.)	Thermo-e.m.f. (μV.)	Thermo-electric power (μV./°C.)
100	575	4·76	375	2825	9·60
150	813	5·48	387	2940	10·40
200	1087	6·76	400	3075	11·45
250	1425	9·50	412	3212	13·60
300	1900	10·4	424	3375	15·90
312	2025	13·5	435	3550	20·00
325	2200	14·6	445	3750	21·20
337	2375	16·0	455	3962	23·70
350	2575	10·4	464	4175	25·00
362	2700	9·60	472	4375	

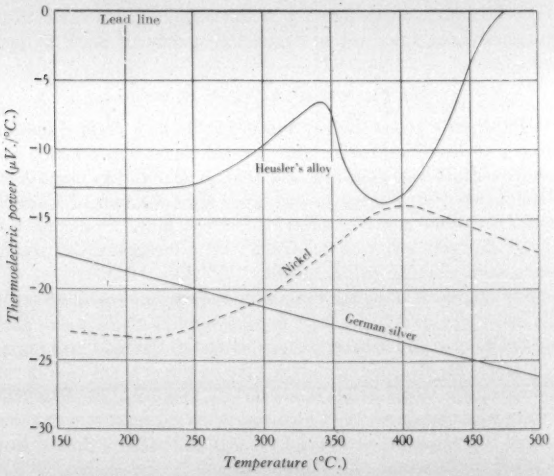

Figure 2.

electromotive force took place between 340 and 380° C. and subsequent careful observations, extending from the lowest to the highest temperatures, confirmed this. Table 1 gives the results arrived at with rising temperatures. German silver is strongly negative to lead and although the alloy is positive to German silver it is not

sufficiently so to make it positive to lead until temperatures approaching 500° C. are reached, as will be seen in figure 2, where the curve of thermoelectric power is traced relative to the zero line of lead which it crosses about 479° C. At higher temperatures than this the alloy no doubt becomes positive to lead.

The salient feature of the curve is the double inflection comprised between temperatures of 340 and 385° C.; the mid-temperature of 362° is close to the temperature which is the critical point for magnetism and where the discontinuity occurs in the specific heat.

In figure 2 the straight line representing the thermoelectric power of German silver relative to lead is drawn, and also, for the sake of comparison, the curve of thermoelectric power of nickel relative to lead. Nickel exhibits a change of 9 or 10 microvolts per degree in an interval of 200°, whilst the alloy performs an oscillation very little less, but in an interval of temperature of no more than 50° or 60°. The trend of the two curves is in opposite directions.

§ 7. THE SPECIFIC HEAT OF HEUSLER'S ALLOY

The specific heat of ferromagnetic substances exhibits features which are peculiar to such bodies. All the strongly ferromagnetic substances have an abnormal increase of the true specific heat with rise of temperature up to the critical temperature and at or near this point a brusque diminution to a lower value. This discontinuity has an interesting bearing on the theory of ferromagnetism.

Heusler's alloy when put to the test of experiment is found to conform to other strongly ferromagnetic bodies in the behaviour of its specific heat[5]. The experiments on the alloy here described were carried out by a calorimetric method. The alloy broken into small pieces was heated in a quartz tube round which was wound a spiral of high-resistance wire. The strength of the current passed through this spiral could be increased so as to raise the temperature of the interior of the tube to 500° C. or more if required. Both ends of the tube were closed but it was arranged that one end could be momentarily opened to allow the contents of the tube to be emptied into the calorimeter. During the heating the tube was kept in a horizontal position, but when the moment arrived for transferring the heated alloy to the calorimeter a swift movement turned the tube into the vertical position to let the alloy drop into the calorimeter. Temperatures were read on a thermocouple in the heater and on a finely graduated thermometer in the calorimeter. Thirty-nine experiments were made at different temperatures to determine the mean specific heat between the selected temperatures and about 15° C.

Table 2 and figure 3 show the mean specific heat. The accuracy of these measures only allows the fourth decimal place to be estimated, but this is more than sufficient to demonstrate the general conformity of Heusler's alloy to other ferromagnetics.

Table 2

Temperature (°C.)	100	300	325	349	356	360	364	375	389
c_m	0·1170	0·1241	0·1265	0·1268	0·1297	0·1303	0·1308	0·1311	0·1316

A method due to Dumas, and used by Pierre Weiss[11], permits the calculation of the true specific heat to be made at any temperature. If c_m is the mean specific heat and C the true specific heat at temperature T then

$$C = c_m + \frac{dc_m}{dt}(T - t),$$

where $(T-t)$ is the interval of temperature used in calculating the true specific heat.

It is in the vicinity of the critical temperature that the true specific heat is of interest. Careful determinations near this point and calculations carried out according to the above formula give the true specific heat, at or just below the critical temperature, as 0·1786 and, just above, as 0·1426. The difference, ΔC, the discontinuity, is therefore 0·036.

Thus Heusler's alloy shows the same typical features as other ferromagnetics in the specific heat when the temperature rises to high values. Table 3 is given[6] for comparison.

Table 3

	Fe	Co	Ni	Heusler's alloy	Fe_3O_4
C_θ ...	0·306	0·290[6]	0·158[7]	0·179	0·299
ΔC ...	0·120	0·118	0·032	0·036	0·079

§ 8. THE SPECIFIC HEAT OF MANGANESE AT HIGH TEMPERATURES

The specimen of manganese used in the following experiments had a purity of 98 per cent, the impurities being chiefly carbon and a little iron. It was hard, rather brittle and not readily acted upon by the air. Determinations of the mean specific heat between two temperatures were made by a calorimetric method and from such determinations the true specific heat was derived as described above in the section dealing with the true specific heat of Heusler's alloy. Twenty-five experiments were made and figure 3 traces the results obtained. Nearly all the points are averages of the results of two and three experiments between the specified temperature and 15° C.

The curve in figure 3 indicates very clearly that the mean specific heat of manganese treated as a function of the temperature suffers a sharp change in direction at about 350° C. and that there is at this temperature a large discontinuity in the true specific heat. It would appear from this that there is a critical temperature at 350° C.

The curve also shows that the true specific heat at this temperature is 0·274 and, just above, it falls abruptly to 0·149 which gives a discontinuity (ΔC) of 0·125. These are values of the same order as are found in iron.

The rapid rise of the true specific heat and the discontinuity at a critical temperature are all marked features of ferromagnetic materials, particularly the discontinuity which plays a leading part in the kinetic theory of ferromagnetism.

But the metal manganese unalloyed with other metals has never shown itself unequivocally ferromagnetic and the specimen used in these experiments has not exhibited any signs of strong magnetism. Nevertheless manganese united with one or with two other metals of a certain class forms alloys which in general show ferromagnetic properties, in some instances in a high degree, and this suggests that there is a ferromagnetism latent in manganese which can thus be made to exhibit itself. Bates and Pantulu [8] have made a determination of Curie's constant for manganese

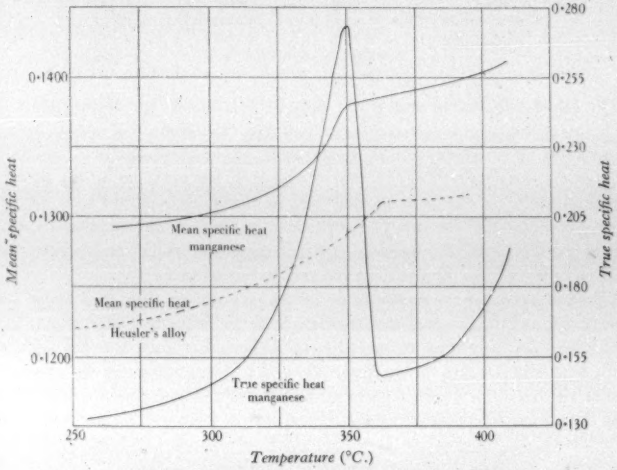

Figure 3. Mean and true specific heat of manganese.

and from this and other considerations the intensity of magnetization of the unalloyed metal may be expected to be of a high order, which would also be consistent with the large discontinuity in the true specific heat of the metal. But if future experiments finally decide that manganese is to be classed as non-ferromagnetic then the large discontinuity of the true specific heat of this metal may necessitate a revision of that part of the theory of ferromagnetism which attributes the discontinuity to the loss of an immense intrinsic magnetic field.

§ 9. THE HEAT CAPACITIES OF THE CONSTITUENTS OF THE ALLOY

The work of Neumann and Kopp and others has shown that the molecular heat of a compound can be treated as the sum of the atomic heats of its constituents and Regnault has extended the rule similarly to alloys. It is of great interest to apply this law to Heusler's alloy and to inquire whether the high true specific heat

of the alloy at its critical temperature is to be found in one or more of its constituents.

Beginning at air temperature we have the following values:

Table 4

	Percentage	Specific heat	Percentage heat
Copper	59·2	0·090	5·328
Aluminium	17·6	0·212	3·731
Manganese	23·3	0·122	2·843
	100·1		11·902

The calculated specific heat of the alloy is therefore 0·119. Experiments show it to be 0·117 which is in fair agreement with the calculation and is a confirmation of Regnault's rule. At the critical temperature of the alloy, the true specific heat of copper may be put at 0·113 and that of aluminium at 0·250 according to reliable determinations[9, 10]. The true specific heat of manganese should then be of the order 0·3 in order that the sum of the percentage heats of the constituents may be equal to the total heat of a hundred parts of the alloy, which, as has been shown above, is 17·86 calories for 100 g. at the critical temperature.

A determination of the true specific heat of manganese described above shows it to be 0·274 at 350° C. which is rather less than the estimated value of 0·3. Just a little higher than the critical temperature the experiment leads to 0·149 as the true specific heat which makes the discontinuity 0·125. Using these results we can now calculate the heat of a hundred parts of the alloy as follows:

At the critical temperature we have

	Percentage	True specific heat	Percentage heat
Copper	59·2	0·113	6·69
Aluminium	17·6	0·250	4·40
Manganese	23·3	0·274	6·38
	100·1		17·47

and just above the critical temperature

	Percentage	True specific heat	Percentage heat
Copper	59·2	0·113	6·69
Aluminium	17·6	0·250	4·40
Manganese	23·3	0·149	3·47
	100·1		14·56

These calculations make the true specific heat of the alloy at its critical temperature 0·175 compared with 0·179 by a direct determination, and just above the

critical temperature 0·146 compared with 0·143 from experiments on the alloy itself. The calculation assumes that manganese preserves its true specific heat when alloyed with other metals.

If magnetite be treated in the same way it may be shown that the very high true specific heat of iron of 0·306 at its critical temperature is preserved in the compound magnetite (Fe_3O_4) at its critical temperature. The truth of this is seen in the following table in which the composition is expressed in percentages. At the critical temperature we have

	Percentage	True specific heat	Percentage heat
Iron	72·3	0·306	21·91
Oxygen	27·7	0·275	7·62
	100·0		29·53

and just above the critical temperature

	Percentage	True specific heat	Percentage heat
Iron	72·3	0·186	13·45
Oxygen	27·7	0·275	7·62
	100·0		21·07

This calculation gives the true specific heat of magnetite at its critical temperature as 0·295 in comparison with 0·299 by direct experiment, and just above the critical point 0·211 as against 0·217 found from experiments on magnetite itself.

It appears that the high true specific heat of iron, which occurs in the pure metal at 785° C., is preserved in the compound magnetite at its critical temperature of 580° C., a temperature which is rather more than 200° below that of iron in the uncombined state.

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DISCUSSION

L. F. Bates. I should like to point out that the use of the equation

$$C_a/C_n = K_a(T-\theta_a)/K_n(T-\theta_n)$$

postulates a linear variation of the reciprocal of the susceptibility with temperature for both nickel and Heusler alloy above their paramagnetic Curie points. Now it seems quite certain that a linear variation in the case of nickel does not exist in the temperature-range under consideration, and I do not know of any experiments which show a linear range in the case of Heusler alloy. Moreover, the temperatures θ_n and θ_a as defined by the author are not the paramagnetic Curie points which occur in the statement of the Curie-Weiss law, and θ_n should be replaced by a temperature some 15° higher, while θ_a should presumably be replaced by a temperature about the same number of degrees higher, even if approximately linear relations are assumed.

Bates and Pantulu, in measuring the susceptibility of amorphous manganese, did not make measurements above 350° C., but they found no evidence of a marked break in the magnetic properties at 350° C. It therefore appears to me that some change in structure at 350° occurred in the case of the authors' specimen of manganese, and here X-ray data would help. The conclusions in the final portion of the paper appear to me to be based on an incomplete survey of the available data, for the results obtained with manganese arsenide are certainly not in agreement with them.

Author's reply. The points referred to by Dr Bates in connexion with Curie's constant have not been overlooked, but there seems to be some divergence of opinion on the methods of obtaining the constant following the Weiss modification of the Curie law. Certain considerations, however, lead to a calculated value which is not far from that in the paper and which makes it acceptable.

Dr Bates's interesting and valuable researches on manganese arsenide do not invalidate what has been set out in the final part of the paper, but show that this substance has a behaviour all its own.

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ON A NEW TYPE OF ELECTRONIC OSCILLATOR TUBE WITH PARALLEL PLANE GRIDS

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ABSTRACT. The paper describes results obtained with an experimental tube, the electrode system of which consisted of two parallel plane grids with two symmetrically arranged cathodes external to them. When Lecher wires were attached to the two grids, oscillations could be obtained either (A) with the tube used as a triode, potentials being applied to the grids in the usual way for the production of Barkhausen-Kurz oscillations, or (B) with both cathodes emitting and the two grids at the same positive potential. The longest waves generated with the B connexion satisfied the relationship $\lambda^2 v_g = \text{constant}$.

For both A and B the wave-lengths of the generated oscillations were determined almost entirely by the length of the attached Lecher wires.

The behaviour of the B system showed some resemblance to that of a relaxation oscillator maintaining, and coerced in frequency by, a vibrator of small damping.

§ 1. INTRODUCTION

Some time ago Dr Eccles suggested to me that it might be possible to produce electronic oscillations in a tube having electrodes arranged as shown diagrammatically in figure 1.

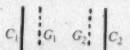

Figure 1. C_1, C_2 cathodes; G_1, G_2 grids.

C_1, C_2 represent two cathodes outside two plane electrodes G_1, G_2 to which a positive potential could be applied. The electrodes G_1, G_2 being of grid construction, space charge would accumulate in the otherwise field-free region between them, and oscillations should be maintained in a suitable Lecher wire circuit attached to the two grids.

A tube was made up and tested in March 1934. Lately, experiments have been made with a view to repeating and extending the results then obtained, a demountable Pyrex tube with movable electrodes being used. It was originally intended to defer the publication of the results given in the present paper until they had been verified and amplified with this new apparatus. However, work has been recently carried out on a plane-electrode demountable triode[1], some of the results of which appear to accord with those I obtained by using the original double grid tube as a triode. It seems likely to be of interest, therefore, to record now the behaviour of the double-grid tube, used both as a triode and in the manner for which it was in the first place designed.

§ 2. DESCRIPTION OF APPARATUS AND PROCEDURE

The arrangement of the electrodes in the experimental tube is shown in figure 2. The cathodes consisted of W-shaped filaments of tungsten wire kept taut by small spirals of molybdenum wire, in quartz frames. The latter were held in position by the lead-in wires.

The grids, of copper gauze with a transparency of 50 per cent, were also supported by stout copper leads and the platinum-glass seals. The cathode connexions were led out of the glass envelope on the opposite side from the grid leads, both sets of leads being horizontal.

The apparatus was connected through wide tubing, fitted with a large tap, to a Metropolitan-Vickers oil condensation pump, backed by a Hyvac pump. Apiezon

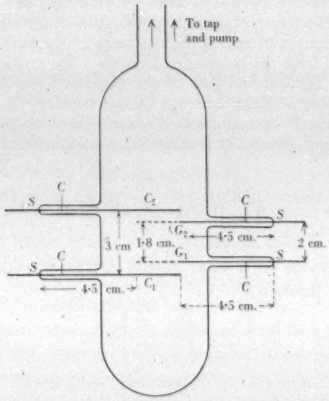

Figure 2. C_1, C_2 cathodes; G_1, G_2 grids (copper gauze 2 cm. square); S, S platinum-glass seals; C, C copper leads.

L grease was used for the tap, and for sealing the flat ground-glass-steel joint at the top of the pump.

The tube was baked out at 160° C. and the filaments were electrically heated while pumping proceeded. This treatment was repeated until the tube, itself used as an ionization gauge, showed little or no trace of residual gas. Before experiments were made on any particular day, the glowing and pumping-out processes were continued until consistent and repeatable results were obtained in determining the tube characteristics. The plot of log (grid current) against log (grid voltage) then showed a slope of $\frac{3}{2}$, with sufficient filament emission.

It was found that with a Lecher-wire system of suitable length attached to the two grids, and with one emitting cathode, Barkhausen-Kurz oscillations could be obtained with the greatest ease. These oscillations were utilized to heat the grids and remove traces of residual gas. The Lecher-wire system connected to the two

grids consisted of two parallel wires of stranded phosphor bronze, soldered at one end to two short copper pins passing through and firmly held by two vertical ebonite pieces supported by a wooden block. This block was fixed on a wooden baseboard along the edges of which two wooden strips were fastened to form a groove. The copper pins were at the same horizontal level as the leads from the two grids, and were soldered directly to the platinum wires leading out through the tube extensions. The phosphor-bronze wires passed through two holes in a copper plate about 8 in. square, which was supported in another wooden block which could slide in the groove. The holes were partially blocked by ebonite rings, with small copper tubes fitted through them. A blocking condenser was connected to the two tubes. The Lecher wires passed through these tubes, making contact with them, and then through holes in an ebonite piece fastened vertically on a third wooden block which was fixed to the baseboard. The effective length of the Lecher-wire system was altered by movement of the block carrying the condenser bridge and reflecting plate.

A Lecher-wire system could also be connected to the two cathodes when desired. In general, however, the positive ends of the cathodes were connected through a 0·003-μF. condenser, the negative ends being connected directly to each other.

§ 3. EXPERIMENTAL RESULTS

(A) *Tube used as triode.* Either triode (one cathode emitting) would oscillate very easily when the nearer grid was made positive and the outer grid was at some potential near that of the cathode. Oscillations for given values of inner grid voltage v_{g1} and outer grid voltage v_{g2} occurred over quite a large range of Lecher-wire length. For example, with v_{g1} equal to 160 V., v_{g2} equal to -2 V., and i_{g1} equal to 2 mA., oscillations occurred over a range of Lecher-wire length, measured from the middle of the electrode system, of 100 → 24 cm. When the Lecher-wire bridge was pushed steadily in towards the tube the amplitude at first increased, then suddenly dropped to zero at one particular point, and afterwards rose again.

It was observed that the current to the positive grid was always diminished when oscillation set in; in general this diminution was much greater than the resultant current to the outer electrode.

In one series of experiments, the Lecher wires connected to the grids were kept at a constant length of 63 cm. and it was found that the generated wave-length did not vary by as much as 2 per cent from the value 3·02 metres, although oscillations could be detected with v_{g2} varying from -6 to $+2$ V., and v_{g1} from $+98$ to $+184$ when $v_{g2}=-2$. The triode was working on the steep part of the $\{v_{g1}, i_{g1}\}$ curve, but nearer the top than the bottom bend.

With v_{g2} equal to -2, as also with v_{g2} equal to $+2$, the oscillation-intensity, as measured by the deflection of the galvanometer in the wave-meter circuit at resonance, increased steadily with increase of v_{g1}.

In another set of experiments, in which a Lecher-wire circuit was attached to the two cathodes, the optimum position of the bridge on the grid side was

independent of v_{g1} and v_{g2} over a considerable range. The position was affected appreciably by the filament emission.

(B) *Tube used with v_{g1} equal to v_{g2} and both cathodes emitting.* It was found that oscillations could be obtained with this arrangement only when the vacuum in the tube was very good. It was necessary to pump out the tube for some time, and advisable to heat the electrodes by generating high-frequency oscillations with the A form of connexion before making the experiments.

In favourable circumstances oscillations of very good amplitude could be obtained with the two grids at the same positive d.-c. potential. The tube generated oscillations best when the emission currents from the two cathodes were equal. In all cases the onset of oscillation was accompanied by a diminution in both grid currents.

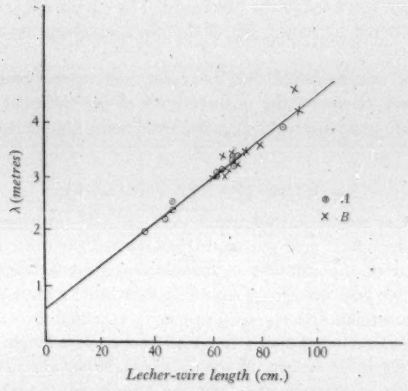

Figure 3.

In general, for fixed values of grid-potential and filament emission the range of Lecher-wire length for which oscillation would occur was very much smaller than for the A connexion. When the Lecher-wire length was steadily diminished the amplitude of oscillation increased and then abruptly stopped, and oscillations could not be restarted by further reduction of the effective Lecher-wire length.

When oscillations of large amplitude were being generated, it was sometimes found that touching either of the grid leads stopped the oscillations. They could be restarted by breaking and then re-making the connexion of the h.t. battery.

In figure 3 is shown the linear relation between Lecher-wire length (measured from the middle of the electrodes to the bridge) and the generated wave-length, for A experiments in which $v_{g1} \neq v_{g2}$ as well as for B experiments in which $v_{g1} = v_{g2}$. Figure 4 shows the relation between the wave-length generated and the voltage in case B. The wave-lengths were measured by means of a long Lecher-wire wave-meter, with crystal detector and galvanometer [2] or by means of an absorption

wave-meter[3]. Other wave-lengths for the B arrangement were determined from a graph of $\{v_g, L\}$, figure 5, where L represents length of Lecher wires measured from the middle of the electrodes to the bridge, and from the $\{L, \lambda\}$ graph of figure 3. This procedure was justified by the results of experiments in which the Lecher-wire length was kept constant. For example with a Lecher-wire length of 94 cm. v_g could be changed from 148 to 176 V., i.e. over the whole range of v_g for which oscillation occurred, without producing any detectable change in wave-length.

Notes on the results. It was not possible, owing to the final puncturing of the glass envelope, to make a complete comparison between the behaviour of the tube when used in the A or in the B manner; however, with other circuit conditions the

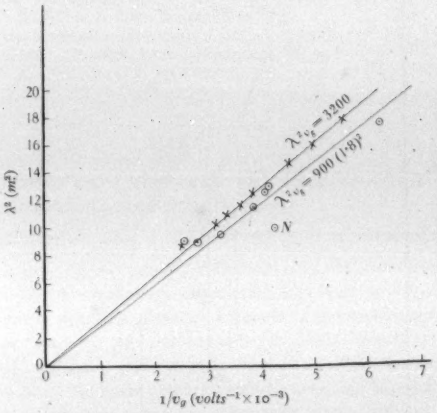

Figure 4. Points × are from figures 3 and 5.

same, both cathodes emitting, and a definite value for v_{g1}, changing over from the B method to the A method ($v_{g2}=0$) involved shortening the Lecher-wire length for maximum oscillation—i.e. oscillations of longer wave-length were more readily maintained with the B arrangement. With the A connexion, oscillations were obtained when the grid current was limited either by space charge or by emission; with the B connexion, oscillations started when the grid currents were just emission-limited. It will be seen from figure 4 that all points except those corresponding to non-restoring conditions lie near the line for which $\lambda^2 v_g = 900\,(1{\cdot}8)^2$. This relation gives the wave-lengths calculated from $\lambda = 2cT$, where λ is the wave-length in metres, $c = 3 \times 10^8$ m./sec., and T the time of transit between G_1 and G_2 assuming a virtual cathode halfway between G_1 and G_2, and full space charge. It is not certain, however, that these conditions actually held for the experiments; further work is desirable to clear up this point. It was found that the Lecher-wire circuit

between G_1 and G_2 was much more critically effective in controlling the frequency of oscillation than an additional Lecher-wire circuit between the two cathodes.

The results show the possibility of obtaining electronic oscillations with a new arrangement—a Lecher-wire circuit connected to two plane grid-form electrodes initially at the same positive potential and capable of collecting electrons from two symmetrically arranged external cathodes. The mechanism of maintenance has not

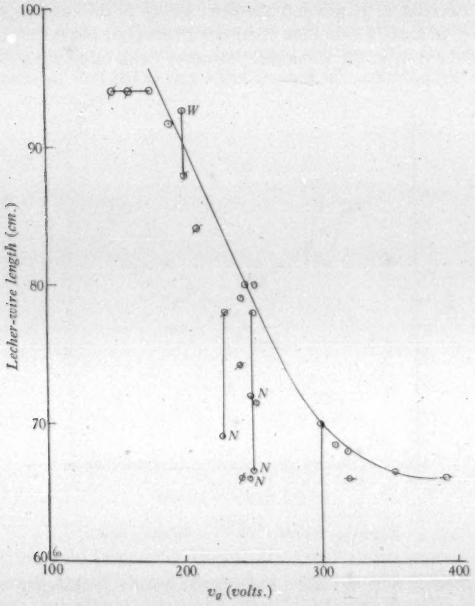

Figure 5. Lines show range of oscillation. ⊙ good amplitude, restoring; ⊙*N* non-restoring; ⊘ not tested as regards restoring conditions; ⊙*W* very weak oscillation.

yet been fully determined, but the results suggest that the effective oscillation of electrons is between and just beyond the two grids.

It is perhaps significant that in many experiments it was observed that the strongest oscillations were obtained for non-restoring conditions, and for the shortest possible lengths of Lecher wire, the circuit being otherwise unchanged. There appears to be some analogy between this result and the coercing of a relaxation oscillator by a coupled vibrator of small damping, like that which occurs, for example, in the neon-lamp tuning-fork circuit[4,5].

§ 4. ACKNOWLEDGMENTS

I should like to express my thanks to Dr W. H. Eccles for suggesting the work and for his interest in its progress.

The experiments were carried out in the Physics Laboratory of the London (R.F.H.) School of Medicine for Women. My thanks are also due to the Council of the School for a grant from the Waller Research Fund for the purchase of apparatus.

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DISCUSSION

DR L. HARTSHORN asked whether the author had any clue to the reason why oscillations occur under the conditions described.

LORD RAYLEIGH asked what would be the effect of an extraneous magnetic field.

AUTHOR'S replies. In reply to Dr Hartshorn: An explanation of the method of maintenance of the B oscillations must take into account the following facts: (1) the grids were at or near a potential antinode of the oscillations in the Lecher-wire system (see figure 3); (2) oscillations began when the grid currents were just emission-limited, and both grid currents were diminished at onset of oscillation; (3) for a given value of the static potential applied to G_1 and G_2, oscillations could be obtained over a considerable range of Lecher-wire length, and the generated wavelength was determined by the latter; for the longest waves generated $\lambda^2 v_g$ had a value which corresponded with the relation $\lambda = 2cT$, where T was equal to the time of transit of an electron either from G_1 to G_2 under full space-charge conditions, or from F_1 to F_2 with full space charge between F and G, and negligible space charge between G_1 and G_2. It seems probable that the modes of maintenance of the A and B oscillations may be similar in nature; in each case two electron streams travel in opposite directions, and it may be supposed that periodic changes in electron-density either initiated or intensified by the variations of potential of G_1 and G_2 arrive at these electrodes in the appropriate phase for maintenance of oscillation. For case B the source of these periodic changes in electron-density is not likely to be a succession of pendular oscillations of groups of electrons between the two cathodes, since the effective grid-transparency would be only 25 per cent, being 50 per cent for each grid.

The present results do not enable one to discriminate completely between two other possible methods of maintenance: (*a*) Negative-conductance effects due to

the transit times of disturbances in the electron streams in the paths C_1, G_1, G_2 and C_2, G_2, G_1 respectively. The time of transit from G_1 to G_2 should, in this case, be equal to approximately one-half, and that from F to G approximately one-quarter, of the periodic time of the Lecher-wire oscillations. (*b*) A periodic supersaturation with space charge of the G_1, G_2 space, with successive discharges in the G_1 and G_2 directions respectively. The interval between successive discharges would be equal to half the periodic time of the Lecher-wire oscillations. The fact that the periodic disturbances in the electron streams can be coerced over such wide frequency ranges (see figure 5) suggests that they are probably of relaxation rather than of sinusoidal form.

In reply to Lord Rayleigh: The effect of a magnetic field on the generation of oscillations by the original tube was not tried. Apart from the use of an axial magnetic field in the generation of electronic oscillations by the cylindrical diode used as a magnetron, it has been shown by a number of experimenters that the effect of such a magnetic field on the oscillations generated by commercial triodes in the usual Barkhausen-Kurz circuit is to produce effects similar to those brought about by a decrease of the plate potential. If either of the tentative explanations given in the preceding paragraphs of the mode of generation of the B oscillations is correct, the presence of a transverse magnetic field might be expected to hinder or stop oscillation, since no reversal of electron-path is supposed to occur in the absence of a magnetic field. A longitudinal field would have a focusing effect on the electron streams. Some electrons not initially travelling parallel to the axis of symmetry of the electrode system would spiral about the magnetic lines, and therefore would remain for a longer time between the electrodes. These would increase the normal space-charge density and might favour the production of oscillations if explanation (*b*) is the correct one. I hope in the future to try the effect of an extraneous magnetic field on another experimental tube with an electrode system similar to that of the original one, and generating oscillations in the same way.

535·551

THE VARIATION OF DOUBLE REFRACTION IN CELLULOID WITH THE AMOUNT OF PERMANENT STRETCH AT CONSTANT TEMPERATURE AND AT DIFFERENT TEMPERATURES

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ABSTRACT. Different specimens of celluloid (xylonite) were stretched beyond the elastic limit, so that they had produced in them amounts of permanent stretch which differed from one specimen to another. The residual double refraction at constant temperature was measured in each specimen at a number of wave-lengths in the visible spectrum, and the dispersion in every case was found to follow the law $n/\lambda^2 = A - B\lambda$, where n is the permanent double refraction in wave-lengths at the wave-length λ and A and B are constants for the particular specimen. It was found also that in each specimen n had a maximum value at some wave-length λ_M, the values of λ_M being less in those specimens which had smaller permanent stretches than in those which had larger permanent stretches. Observations were made on the effect produced on the dispersion and on the values of λ_M by increase of temperature.

§ 1. INTRODUCTION

Some years ago, S. R. Savur[1] showed that the dispersion of the residual double refraction in celluloid produced by permanent stretch changes with the amount of such stretch, and becomes increasingly anomalous as the permanent stretch increases.

Earlier than this, however, M. Wachtler[2] had carried out a series of experiments in which he found that the residual double refraction changes sign as the permanent stretch increases. No such change of sign was observed by Savur, and considerable doubt was expressed by him as to the accuracy of Wachtler's work. Similar doubt was also expressed by Ramspeck[3], but Wachtler later denied that any inaccuracy had occurred in his work. He stated however that he used a celluloid having a large content of camphor. Quite recently Derksen and others[4] have investigated the change in the double refraction of celluloid with variation of camphor-content. Their results show that for celluloid in which the camphor-content is less than about 35 per cent the double refraction produced by overstrain is entirely positive, whilst for celluloid with a camphor-content of more than 40 per cent such double refraction is entirely negative. For one particular case, however, in which the camphor-content was exactly 40 per cent—the same as that used by Wachtler—the double refraction is positive for small overstrain, while for large

overstrain it is negative. The change of sign occurs for a stretch of about 8 per cent. Now the celluloid used by Savur had a camphor-content of about 24 per cent.

Hence it would appear certain that Wachtler and Savur were both right in their results, and the apparent discrepancy can be fully explained by the fact that they were using specimens of celluloid containing widely different amounts of camphor.

The present research was undertaken to find firstly the actual law of dispersion of residual double refraction in permanently overstrained celluloid, and secondly what change if any is produced in this dispersion by change of temperature. The celluloid used throughout was supplied by the British Xylonite Co., Ltd., and has the same camphor-content as that used by Savur, namely 24 per cent.

§ 2. PREPARATION OF THE SPECIMENS

Each specimen, cut from a sheet of xylonite 7 mm. thick, was of the approximate dimensions shown in figure 1. When the specimen was put under tension, a uniform stress was produced in the central portion *CD*. Throughout the parts *BC* and *DE* the stress changed fairly rapidly, and in the parts *AB* and *EF* it became quite small towards *A* and *F* except very near the holes where the load was applied. Each specimen was then placed in turn in the straining apparatus shown in figure 2. The knife-edge *A* being fixed, tension was applied by raising *B* until the desired amount of double refraction was produced in the centre of the specimen. As the specimen stretched, *A* and *B* both remaining fixed,

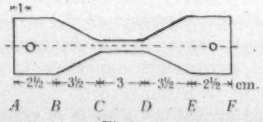

Figure 1.

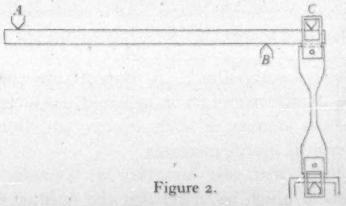

Figure 2.

the tension automatically decreased and hence *B* had continually to be raised to maintain the double refraction as required. In cases where a high residual double refraction had to be produced the tension had to be applied continuously for several weeks, and hence any risk of breakage during the times when the specimen was not under observation was reduced to a minimum by this method.

After release of the tension the specimen was left for several years, so as to ensure that all time creep in the residual double refraction had either ceased altogether or at any rate become negligible when placed between crossed nicol prisms in sodium light; the specimen then had an appearance similar to that shown in figure 3.

The numbers 0, 1, 2, ... refer to the order of the respective double-refraction bands. Thus the integral part of the residual double refraction in the central

section of each specimen could easily be determined merely by counting these bands.

Altogether seven specimens were prepared in this way, having at their central sections residual double refractions varying respectively from about $0{\cdot}4\lambda$ to 7λ (at $\lambda = 5896$).

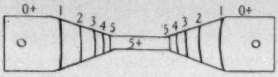

Figure 3.

§ 3. METHOD OF EXPERIMENT AT CONSTANT TEMPERATURE

The method used was the improved spectroscope method[5]. A preliminary set of observations had shown that an observable shift of the bands in the spectroscope was produced by a change in temperature of 1° C. in the specimen, and also by a change of 3° C. in the temperature of the quartz plate. It was therefore neces-

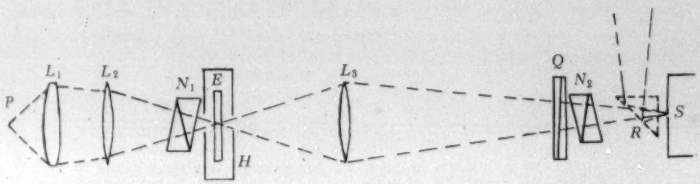

Figure 4. *P*, Point-o-lite; N_1, N_2, nicol prisms; *H*, heater; L_1, L_2, L_3, lenses; *E*, specimen; *Q*, quartz plate; *S*, slit of spectrograph; *R*, prism (removable) for iron spectrum.

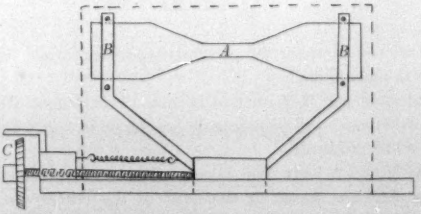

Figure 5. *A*, specimen; *BB*, clamps holding specimen; *C*, micrometer screw head.

sary to take precautions to keep the temperatures of both specimen and quartz plate constant within these limits. Moreover, as was to be expected from the nature of the material even in the central section of the specimen, the residual double refraction was found to vary slightly from point to point. An enlarged image of the central section was therefore produced on the slit of the spectroscope by means of a suitable lens system, the arrangement of the apparatus being as in figure 4. The specimen was mounted rigidly as in figure 5, and together with

its support it was entirely enclosed in a small electric heater so that it could be maintained at any desired temperature. By this means errors due to any movement of the specimen or change in its temperature during the progress of a set of observations were avoided. The time taken for each set of observations was about $\frac{3}{4}$ hour, and during that time the temperature of the room, and hence that of the quartz plate, in no case varied by more than 2° C.

The procedure was in all cases as follows. The room-temperature being steady at about 19° C., the cross wires of the spectroscope were set at a particular wave-length, the iron arc spectrum being used as a standard. Then the reading of the screw head of the quartz plate[6], necessary to bring into a band coincidence with the cross wires, was observed, *the specimen not yet being in position*. This was repeated for eleven different wave-lengths between 6500 and 4900 A. Outside this range accuracy of setting was not possible, the bands not being sufficiently well defined.

The specimen was then placed in position in the heater, the temperature of which was raised from that of room-temperature to 28° C. in 1 hour and then maintained constant for a further $\frac{1}{2}$ hour, after which the observations were repeated. From these two sets of observations the values of the residual double refraction n (in wave-lengths) at a temperature of 28° C. were calculated for each of the eleven wave-lengths.

n

§ 4. EXPERIMENTAL RESULTS AT CONSTANT TEMPERATURE

The values of n are shown in table 1. An attempt was then made to find, if possible, a law of dispersion of n, and it was found that the observations were best fitted by the equation:

A, B

$$\frac{n}{\lambda^2} = A - B\lambda \qquad \text{.....(1),}$$

λ

where A and B are constants for the particular specimen under observation, and λ the wave-length in angstroms.

When the values of n/λ^2 were plotted against λ a very good straight-line graph was obtained in every case, and these graphs are shown in figure 6. The lines do not meet in a point when produced.

The values of A and B were then calculated for each specimen by the method of least squares, and are shown at the head of the corresponding columns in table 1. From these values of A and B the corresponding values of n were calculated from equation (1), and these are also shown in table 1 in the columns headed n_1 together with the differences $(n - n_1)$. It will be seen from these differences that the agreement between the observed values n and the calculated values n_1 is very good except for the extreme wave-lengths. We may therefore assume that the law of dispersion of the residual double refraction in permanently overstrained celluloid containing 24 per cent of camphor is of the form $n/\lambda^2 = A - B\lambda$.

n_1

Next the values of n were plotted against λ for each specimen as shown in figure 7. From these graphs it is seen that for each specimen there is one particular

Table 1

λ	Specimen I $A=0{\cdot}629310$ $B=0{\cdot}072124$ $\lambda_M=5816{\cdot}926$			Specimen II $A=0{\cdot}503809$ $B=0{\cdot}057171$ $\lambda_M=5874{\cdot}878$			Specimen III $A=0{\cdot}397844$ $B=0{\cdot}045983$ $\lambda_M=5767{\cdot}987$			Specimen IV $A=0{\cdot}297360$ $B=0{\cdot}034878$ $\lambda_M=5683{\cdot}812$		
	n	n_1	$n-n_1$	n	n_1	$n-n_1$	n	n_1	$n-n_1$	n	n_1	$n-n_1$
6494·993	6·916	6·786	+0·130	5·648	5·589	+0·059	4·279	4·184	+0·095	3·069	2·988	+0·081
6301·524	6·977	6·941	+0·036	—	5·700	—	4·327	4·292	+0·035	3·120	3·080	+0·040
6137·702	7·030	7·031	−0·001	5·739	5·760	−0·021	4·358	4·355	+0·003	3·143	3·138	+0·005
6065·493	7·055	7·058	−0·003	5·748	5·777	−0·029	4·370	4·376	−0·006	3·147	3·157	+0·010
5895·932	7·067	7·093	−0·027	5·760	5·795	−0·035	4·387	4·405	−0·018	3·170	3·188	−0·018
5709·395	7·071	7·090	−0·019	5·772	5·782	−0·010	4·390	4·411	−0·021	3·186	3·202	−0·016
5615·658	7·053	7·073	−0·020	5·764	5·763	+0·001	4·389	4·403	−0·014	3·186	3·211	−0·025
5506·784	7·044	7·040	+0·004	5·737	5·730	+0·007	4·383	4·386	−0·003	3·183	3·193	+0·010
5302·315	6·963	6·941	+0·022	5·666	5·641	+0·025	4·342	4·330	+0·012	3·166	3·161	+0·005
5110·415	6·833	6·809	+0·024	5·553	5·527	+0·026	4·265	4·253	+0·012	3·126	3·111	+0·015
4903·325	6·613	6·628	−0·015	5·355	5·373	−0·018	4·145	4·144	+0·001	3·042	3·038	+0·004

λ	Specimen V $A=0{\cdot}193777$ $B=0{\cdot}023450$ $\lambda_M=5508{\cdot}941$			Specimen VI $A=0{\cdot}140091$ $B=0{\cdot}017424$ $\lambda_M=5360{\cdot}078$			Specimen VII $A=0{\cdot}044343$ $B=0{\cdot}005563$ $\lambda_M=5204{\cdot}626$		
	n	n_1	$n-n_1$	n	n_1	$n-n_1$	n	n_1	$n-n_1$
6494·993	1·832	1·749	+0·083	1·215	1·136	+0·079	0·366	0·346	+0·020
6301·524	1·870	1·827	+0·043	1·247	1·203	+0·044	0·394	0·369	+0·025
6137·702	1·885	1·878	+0·007	1·258	1·249	+0·009	0·397	0·384	+0·013
6065·493	1·896	1·896	0	1·267	1·265	+0·002	0·396	0·390	+0·006
5895·932	1·912	1·930	−0·018	1·281	1·299	−0·018	0·400	0·401	−0·001
5709·395	1·934	1·952	−0·018	1·301	1·324	−0·023	0·405	0·410	−0·005
5615·658	1·937	1·958	−0·021	1·314	1·332	−0·018	0·406	0·413	−0·007
5506·784	1·944	1·960	−0·016	1·318	1·339	−0·021	0·413	0·416	−0·003
5302·315	1·946	1·952	−0·006	1·335	1·341	−0·006	0·413	0·417	−0·004
5110·415	1·944	1·931	+0·013	1·343	1·333	+0·010	0·406	0·416	−0·010
4903·325	1·912	1·894	+0·018	1·336	1·314	+0·022	0·403	0·410	−0·007

λ_M wave-length λ_M for which n is a maximum. Now from equation (1) this value of λ is given by

$$\lambda_M = 2A/3B.$$

These values of λ_M for the different specimens are shown at the head of the N corresponding columns in table 1. Let us denote by N the particular value which n

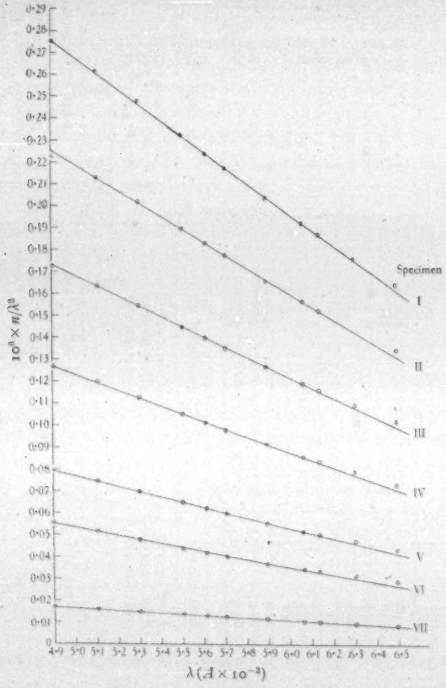

Figure 6.

assumes for λ 5895·932 in any given specimen. Then as N increases from specimen to specimen λ_M is observed to increase.* Again, from figure 7, for those specimens in which $N > 2$ (i.e. in specimens I–IV) the value of n in the red is greater than that in the blue, but in those specimens in which $N < 2$ (i.e. in specimens V–VII) the value of n in the red is less than that in the blue. On examining the specimens in white light between crossed nicol prisms, it was observed that for those specimens

* There is an exception in the case of specimen I, in which there is a slight decrease.

in which $N>2$ the natural sequence of colours is reversed in bands above the second order, whilst this second-order band itself is of a dark purple tint and practically achromatic. This reversal in the natural colour-sequence was observed and explained by Savur.

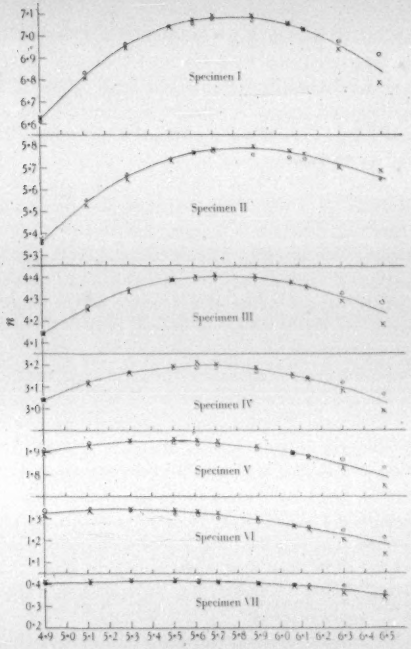

Figure 7.

§ 5. METHOD OF EXPERIMENT AT A SERIES OF TEMPERATURES

The same specimens were used as before, and in each case the following procedure was carried out. After the observations at 28° C. had been made, the temperature of the specimen was slowly raised to 40° C., the time taken being 1 hour. The temperature was then maintained constant for $\frac{1}{2}$ hour and readings were taken as before, but only for four wave-lengths instead of eleven, so as to avoid keeping the specimen at the higher temperature for too long.

A preliminary set of observations on another specimen had shown that at temperatures less than about 50° C. any time creep in the residual double refraction

was negligible. Above this temperature however the time creep increased rapidly with rise of temperature.

The readings at 40° C. having been taken, the temperature was further raised to 50° C., the time occupied being again 1 hour. The readings were then repeated as before.

§ 6. RESULTS FOR A SERIES OF TEMPERATURES

The values of n as calculated from the observations at 40° C. and 50° C. are shown in table 2, together with the corresponding values at 28° C. When the values of n/λ^2 were plotted against λ, straight lines were again obtained, showing that the same law of dispersion holds at the higher temperatures. The corresponding values of A, B and λ_M also are shown.

The results obtained show that n changes with temperature, and hence it is necessary to extend the definition of N, so that N now denotes the value of n for λ 5895·932, the specimen being at a temperature of 28° C. It follows from the results given in table 2 that for each of the specimens I–IV, for all of which $N>2$, the values of n increase as the temperature increases; but in each of specimens VI and VII, for which $N<2$, the values of n decrease as the temperature increases. In the case of specimen V, for which N is very nearly 2, the change in n with temperature is extremely small.

During the preliminary observations mentioned in § 5 it was found that although for specimens in which N is small there is practically complete recovery (i.e. the values of n regain their former values) when the temperature is again restored to 28° C., this is not the case in specimens in which N is large. In such specimens the effect of heating and cooling is to increase the permanent double refraction.

The results for the seven specimens under observation are shown in figure 8, in which the values of n at λ 5895·932 for each specimen are plotted against the temperature. From table 2, it is seen that as the temperature increases the values of the constants A and B increase in specimens I–V, in which $N>2$, but decrease in specimens VI and VII, in which $N<2$. In specimen V the change is very small.

With regard to the change in the values of λ_M with temperature, it is found that as the temperature increases λ_M decreases for specimens I–V but increases in specimens VI and VII. This change in λ_M is to be expected in view of the change in n with wave-length at the different temperatures. At 28° C. the value of n in specimens I–III is greater in the red (λ 6137·702) than in the green (λ 5302·315) but at the higher temperatures, 40° C. and 50° C., the reverse is the case. Owing to observations being made at four wave-lengths only at the higher temperatures, the effect is not well shown in specimens IV and V, although the results tend to show that such is the case. For specimens VI and VII the rise of temperature, although increasing λ_M, does not have such a marked effect on the values of n, which are still less in the red than in the green as was the case at 28° C.

It is quite certain therefore that an appreciable rise of temperature completely changes the character of the dispersion of the residual double refraction, such changes being most marked in specimens for which N is large.

Table 2. Values of the residual double refraction n at different temperatures and different wave-lengths

	Specimen I			Specimen II			Specimen III			Specimen IV		
	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.
A	0·629310	0·621405	0·787973	0·503809	0·593878	0·662430	0·397844	0·452473	0·498440	0·297360	0·337148	0·364428
B	0·072124	0·067710	0·093785	0·057171	0·069995	0·079232	0·045983	0·053473	0·059887	0·034878	0·040838	0·044762
λ_M	5816·926	6118·285	5601·272	5874·878	5656·385	5573·758	5767·087	5641·140	5548·673	5683·812	5503·828	5427·640
n λ 6137·702	7·030	7·573	8·049	5·739	6·210	6·675	4·358	4·697	4·969	3·143	3·312	3·447
n λ 5895·932	7·067	7·627	8·132	5·760	6·283	6·752	4·387	4·754	5·022	3·170	3·349	3·490
n λ 5615·658	7·053	7·642	8·195	5·764	6·311	6·832	4·389	4·791	5·081	3·186	3·383	3·527
n λ 5302·315	6·963	7·586	8·207	5·666	6·278	6·836	4·342	4·758	5·110	3·166	3·367	3·554

	Specimen V			Specimen VI			Specimen VII		
	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.
A	0·193777	0·201627	0·203699	0·140091	0·134411	0·125846	0·044343	0·034960	0·035898
B	0·023450	0·024540	0·024777	0·017424	0·016664	0·015500	0·005563	0·004184	0·004392
λ_M	5508·941	5477·506	5480·863	5360·078	5377·300	5525·161	5204·626	5570·427	5448·998
n λ 6137·702	1·885	1·933	1·961	1·258	1·229	1·166	0·397	0·354	0·344
n λ 5895·932	1·912	1·973	1·991	1·281	1·238	1·190	0·400	0·354	0·341
n λ 5615·658	1·937	1·998	2·020	1·314	1·279	1·217	0·406	0·358	0·355
n λ 5302·315	1·946	2·020	2·045	1·335	1·304	1·233	0·413	0·362	0·354

Some years ago attempts were made, without much success, to anneal celluloid by slow heating and cooling in water. This process merely had the effect of driving off some of the camphor without decreasing appreciably the residual double

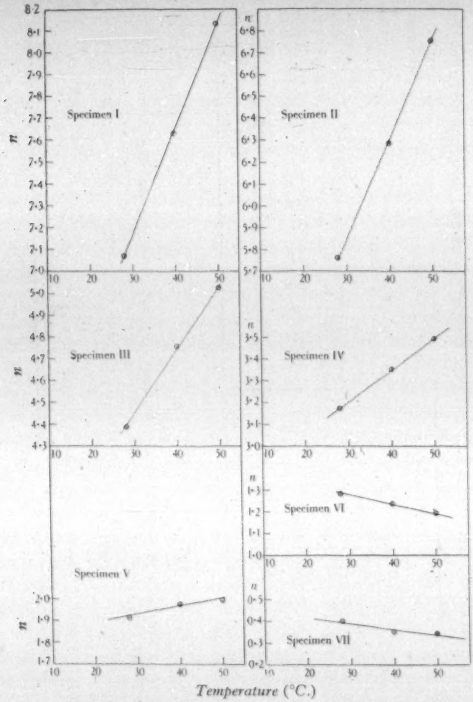

Figure 8. Variation of n with temperature for λ 5895·93Å.

refraction N. The reason is apparent from the results here described, and actually for any specimen in which the residual double refraction N is large such a process will tend to increase and not decrease N.

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DISCUSSION

Prof. L. N. G. Filon. One of the results of the paper is of special importance for photoelastic observations, as it shows why efforts to anneal xylonite by heat treatment have been unsuccessful.

Perhaps the authors could give us information on the following points: (1) whether any double refraction introduced by unequal temperature in the windows of the heater enclosing the specimen is likely to have affected the observations; (2) whether the discrepancies between the observed and calculated values of n in the extreme red, which appear to be shown by figures 6 and 7, are significant and could be accounted for by a modification of the formula (1)—for example, by using a formula of the type $n^2-1=\Sigma A_r/(\lambda^2-\lambda_r^2)$, restricted to a few terms; (3) whether the authors have made any definite observations of the effects of time creep, and, if so, whether the observations show the sense in which this creep operates?

Authors' reply. (1) The glasses used in the windows of the heater were specially selected so as to be free from any initial double refraction. Also they were only attached by soft wax, so that no stress was applied owing to expansion under heat, as might have occurred if they had been enclosed in rigid frames. It is of course always essential to ensure that all lenses, glasses, etc. which are included between the crossed nicols should be free from double refraction. (2) No modification of formula (1) as suggested has been tried as the authors considered the discrepancies between observed and calculated values of n in the extreme red could be accounted for by the comparatively poor visibility in that region. We thank Professor Filon for his suggestion of an alternative formula and will most certainly see if better agreement is obtained by its use. (3) Observations were made at 50° C. on the effects of time creep, with the following results. For specimens in which $N>2$, the double refraction decreased with lapse of time, but even after five hours it was still very much greater than the original value at 28° C. In those specimens in which $N<2$, although the double refraction also decreased with lapse of time, its value after only three hours was much less than the original value at 28° C.

537·533·8

A METHOD OF MEASURING SECONDARY-ELECTRON EMISSION FROM FILAMENTS

By L. R. G. TRELOAR, B.Sc., F.Inst.P. A communication from the Research Staff of the M-O Valve Company Limited at the G.E.C. Research Laboratories, Wembley

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ABSTRACT. A method of measuring secondary emission which may have advantages over the usual methods in certain cases is described. The source of electrons is a tungsten filament mounted axially in a cylindrical grid and anode. The filamentary target is placed parallel to the cathode. With the grid connected to the cathode there is a considerable range of positive potentials V_t and V_a on target and anode respectively for which no secondaries can pass through the grid; under these conditions it is shown both theoretically and practically that the target current i_t is proportional to $\sqrt{(V_t/V_a)}$. This law is then used to determine the primary currents for high values of V_a such that all secondaries emitted from the target reach the anode. These, together with the measured values of i_t, give the secondary emission. The possible effects of high velocity secondaries are considered. Application of the method to tungsten and tantalum gives results in agreement with published data.

§ 1. INTRODUCTION

In the usual method of measuring secondary emission, which has been described by Petry[1] among others, a narrow beam of electrons is allowed to fall on a plate of the material whose secondary emission is to be investigated, this plate or target being surrounded by a collecting-chamber maintained at a suitable positive potential with respect to it. The target must be of such a size that one can be sure that all the electrons in the beam will strike it; then by measuring the currents to the target and to the collector the secondary emission of the target may be obtained. This method does not lend itself readily to the study of the effect on secondary emission of surface contaminations of atomic thickness, for instance of electropositive metals, since the heat treatment of the target necessitates the dissipation of a considerable quantity of energy in the tube, and this is liable to give rise to undesired contamination owing to evolution of gas from the surrounding electrodes or glass envelope. Doubtless this disadvantage could be overcome by means of appropriate modifications, but it would nevertheless be much simpler, from the practical point of view, if a method could be found of using materials in the form of filaments for the measurement of secondary emission, since a filament may readily be raised to a high temperature without any considerable heating occurring in other parts of the tube.

Since it is not possible to produce an electron beam whose thickness would be less than the diameter of a filament, it is necessary to immerse the filament com-

pletely in a stream of electrons and to determine how many electrons will strike it under given conditions. It is the purpose of this paper to show that it is possible, by using a suitable arrangement of electrodes, to determine the magnitude of the electron current to such a filament and the way in which it varies with the relative potentials of the filament and the other electrodes.

§ 2. THE PRINCIPLE OF THE METHOD

The arrangement of electrodes used in this method is shown in figure 1. A is a cylindrical anode, G a concentric grid close to the anode, and C a thermionic cathode. The filament T (referred to subsequently as the target) whose secondary emission is to be studied is stretched parallel to C and at a distance from it of about half the radius of the grid.

If now the grid is maintained at zero potential, potentials being referred to the cathode, and a potential V_t is applied to the target whilst the anode potential V_a is varied, there will be, for a considerable range of V_a, a potential-minimum between T and A which will effectively prevent the passage of secondary electrons either from T to A or from A to T, according to whether $V_t <$ or $> V_a$. It is assumed

V_t, V_a

Figure 1. Illustrating the principle of the method.

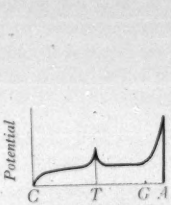

Figure 2(*a*).

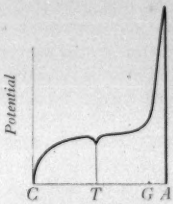

Figure 2(*b*).

Diagrammatic representation of space potentials.

for the present that all the secondaries are emitted with zero velocity; the validity of this assumption will be examined later. It is also assumed that the space charge due to the electrons is negligibly small. The condition in which there is a potential minimum between T and A is represented diagrammatically in figure 2 (*a*), which gives the approximate potential-distribution along a straight line from the cathode through the target and through a space between the grid wires to the anode.

But if the anode potential be sufficiently high the potential-minimum will no longer exist (figure 2 (*b*)). At any point within the grid and not very close to it the combined field due to the anode at potential V_a and the grid at zero potential is approximately equivalent to that which would be produced by an anode at a potential $V_a/(m+1)$ placed approximately at the position occupied by the grid, m being the amplification factor of the grid-anode system. Hence when the anode potential is somewhat higher than $(m+1)\,V_t$ all the secondaries from the target will pass through the grid to the anode.

m

Thus by the use of appropriate anode potentials we can either prevent any of the secondaries from the target from reaching the anode, or cause all of them to reach it, and in neither case will secondaries from the anode reach the target. If now we can find a law relating the current that flows to the target with anode voltage over the region in which secondary emission is absent, we may use this law to calculate the primary current I_p incident on the target in the region in which secondary emission current I_s is present. The current actually measured in the latter case will be $(I_p - I_s)$. Hence we shall be able to determine I_p and I_s.

§ 3. THE RELATION BETWEEN TARGET CURRENT AND ANODE VOLTAGE

Let us imagine the grid to be absent, and let the target filament be assumed to be so small that its field may be considered to be negligible at a distance from it which is small compared with the radius of the anode. The radial flow of the electrons approaching the target in these circumstances may be represented approximately by a flow along parallel straight lines with uniform velocity v (figure 3). The electrons near the target will be deflected into curved orbits, and the current to the target will be proportional to the distance d from the central undeviated orbit to the undeviated portion of the orbit tangential to the target. This distance may be calculated by making use of the fact that the angular momentum of a particle in a central orbit is constant. If v' is the velocity of the particle at the point of contact with the target, we have therefore

$$mvd = mv'a,$$

or

$$d = v'a/v,$$

where a is the radius of the target. Converting the velocities into potentials, and remembering that the current i_t to the target is $2\rho dl$, where ρ is the current-density of the approaching electrons and l is the length of the filament, we obtain

$$i_t = 2\rho al\sqrt{(V_t/cV_a)} \qquad \ldots\ldots(1a),$$

where c is the constant ratio which the space potential in the neighbourhood of T due to the anode bears to the potential of the anode. The presence of a grid at zero potential will change the constant c to c', where

$$(m+1)\,c' = c,$$

and the current is then given by

$$i_t = 2\rho al\sqrt{\left(\frac{m+1}{c}\cdot\frac{V_t}{V_a}\right)} \qquad \ldots\ldots(1b).$$

Thus, in all cases we have $i_t \propto \sqrt{(V_t/V_a)}$.

If we maintain a constant potential on the target and vary the anode potential, the grid being at zero potential, the curve relating target current with $\sqrt{(V_t/V_a)}$ will fall into three parts, which are represented in figure 4. For low values of V_a there will be no secondary electrons passing through the grid. The curve should, therefore, correspond with the theoretical straight line through the origin—AB in figure 4.

This portion of the curve should be the same for all values of V_t. At sufficiently high values of V_a all the secondaries will reach the anode. In this region the primary current will still be represented by the continuation of AB, but the actual current

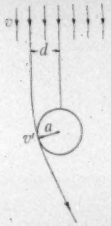

Figure 3. Electron orbits near charged wire.

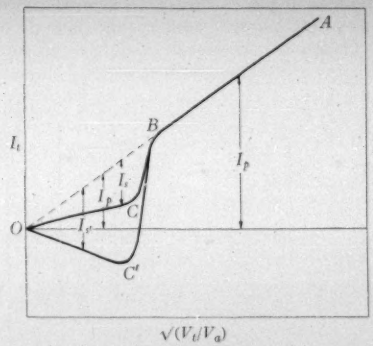

Figure 4. Diagram illustrating the method of obtaining I_p and I_s.

$(I_p - I_s)$ will be another straight line through the origin, since I_s/I_p is constant if V_t is constant. For different values of V_t different lines OC, OC', ... will be obtained. The intermediate portion BC of the curve represents the condition where some but not all of the emitted electrons leave the target. This portion is of no interest for the purpose of measurement.

§ 4. THE PREPARATION OF THE TUBE

We come now to the practical details of the method. A longitudinal section of the electrode system is shown in figure 5. The anode A was a nickel cylinder 40 mm. long and 25 mm. in diameter. The grid G, of diameter 22 mm., was wound with 0·11-mm. molybdenum wire to a pitch of 2·1 mm. on two 0·6-mm. nickel supporting wires. The cathode C was a 0·105-mm. tungsten wire 12 mm. long supported by 0·6-mm. nickel leads. The purpose of making it short was to reduce the effect of irregularities in the field in the neighbourhood of the ends of the electrodes. The target T was, in the first instance, a tungsten filament of diameter 0·105 mm. Both filaments were maintained in tension by springs mounted on wires N and N' attached at the base to the pinch L and at their other ends to the hard glass bead B' which, together with a similar bead B, provided the necessary support for the electrode system. It was found necessary to provide end plates D, D', connected to the grid, having 3-mm. holes for the passage of the wires, to prevent undesirable effects due to charges on the glass bulb. A nickel disc carried a getter pellet H of copper-clad metallic barium which when heated by induction caused a barium deposit to form on the bulb for the purpose of removing residual

gas from the tube. The whole system was sealed into a bulb about 130 mm. long and 40 mm. in diameter.

The tube was pumped with a mercury diffusion pump. After being baked for 10 minutes at 400° C. the electrodes were heated by induction to redness for a few minutes and the getter was dispersed on to the bulb. The tube was then sealed off.

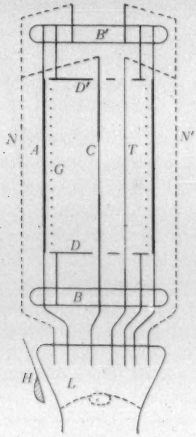

Figure 5. The tube.

§ 5. THE MEASUREMENT OF THE PRIMARY CURRENT

In using the tube it was necessary to avoid space-charge effects. The cathode was, therefore, operated at such a temperature that its emission was saturated. Normally the anode, or anode plus grid, current was maintained in this way at 1·0 mA., and since the fraction of the current arriving at the target was never more than about 1 per cent, this value of anode current was taken to be equal to the total emission from the cathode.

V_g

When the grid voltage V_g was zero and V_t was constant, the variation of the target current i_t with anode voltage was measured. The relation between i_t and $\sqrt{(V_t/V_a)}$ for a number of target voltages is shown in figure 6. It is at once evident that the form of the relation given by equation (1*b*) is satisfied, the points lying roughly on a straight line passing through the origin. The line calculated from the dimensions of the electrodes by means of equation (1*b*) is shown dotted. The fact that the measured currents are 16 per cent higher than the calculated values is probably due to the non-fulfilment of the condition, used in deriving the equation, that the effective field of the target extends over only a very small area. However,

the difference in the numerical constant does not affect the accuracy of the experiments, provided that the relation $i_t \propto V_t/V_a$ is satisfied.

It will be seen that a departure from linearity occurs at about $\sqrt{(V_t/V_a)}=0{\cdot}6$. At this point the anode voltage becomes sufficiently high to draw some of the secondaries through the grid. But we may safely assume that at this and lower values of $\sqrt{(V_t/V_a)}$ the primary current is given accurately by the straight line through the origin.

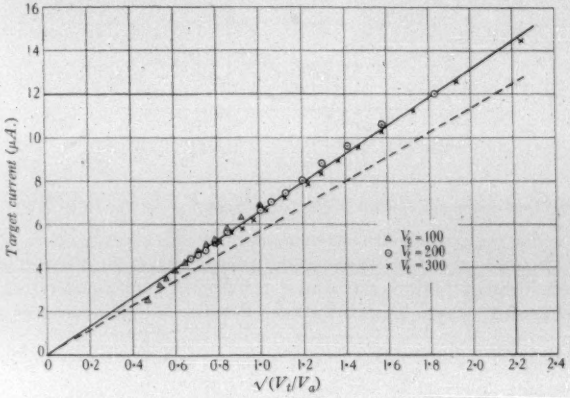

Figure 6. Primary current as a function of electrode voltages.

§ 6. THE MEASUREMENT OF THE SECONDARY CURRENT

In figure 7 the calibrating line for the primary current C obtained in the manner just described is plotted with $\sqrt{\{(m+1)\,V_t/V_a\}}$ as abscissa. Curve B shows the measured values of i_t, when $V_t=50$ V., also plotted against $\sqrt{\{(m+1)\,V_t/V_a\}}$. The difference between corresponding ordinates of curves C and B gives a measure of the secondary current leaving the target at each value of abscissa. It will be seen that from abscissa 1·0 downwards the points on curve B fall very close to another straight line D through the origin. In this region the field is such that all the secondaries emitted from the target are attracted towards the anode; the secondary current is therefore proportional to the primary current, as it should be, and the ratio of the slopes of the straight lines D and C is $(I_p-I_s)/I_p$, from which the secondary-emission coefficient I_s/I_p may be obtained.

At a target voltage of 300 it would be necessary to apply about 1200 V. to the anode in order to draw all the secondaries through the grid. If, however, the grid is connected to the anode about 400 V. is sufficient. A voltage V_{ga} on grid and anode may be converted into a voltage V_a on the anode and 0 on the grid by the relation $V_a=(m+1)\,V_{ga}$.

This method has been verified by the results given in figure 7. Curve *A* shows the target current, taken with the anode and grid connected, when $V_t = 50$ V. Current is plotted against $\sqrt{(V_t/V_a)}$ instead of $\sqrt{\{(m+1)\,V_t/V_a\}}$, which was used as abscissa for curve *B*. Hence for a given value of abscissa the potential con-

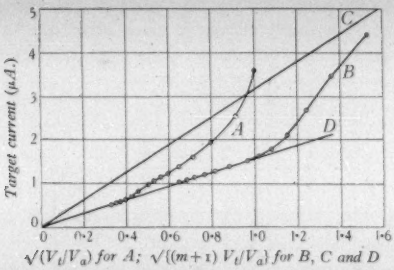

Figure 7. Total current as a function of electrode voltages. $V_t = 50$; $V_g = V_a$ for *A* and 0 for *B*.

ditions within the grid are identical in each of the cases represented by curves *A* and *B*. The line *C*, therefore, represents the primary current for *A* as well as for *B*. Differences between the two curves are due to differences in the amount of secondary emission passing between target and anode. But when all the secondaries emitted

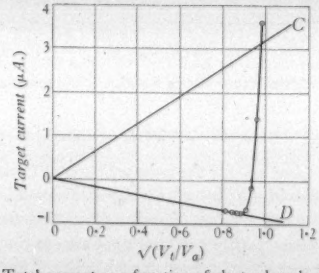

Figure 8. Total current as a function of electrode voltages. $V_t = 300$.

by the target reach the anode and none of the anode secondaries reach the target, the curve *A* approximates to a straight line through the origin. The fact that the same line also represents the saturated secondary emission in the case of curve *B* is a proof of the equivalence of the two methods of measurement.

The curve of secondary emission taken when $V_t = 300$ V. and $V_a = V_g$ is given in figure 8. In this case saturation is obtained when V_a is about 400 V. The negative slope of *D* represents a ratio I_s/I_p greater than unity.

§ 7. APPLICATION OF METHOD TO TUNGSTEN AND TANTALUM

The variation of the secondary-emission coefficient with the voltage of the primary electrons for the case of a tungsten filament (previously heated at about

2800° K. for a few minutes) is shown in figure 9 by the continuous line. For comparison the results obtained by Petry[2] and Krefft[3] by means of the method referred to in § 1 are also given. The differences between the three curves are no greater than would be expected to arise from slight differences in the material or in the state of contamination of its surface.

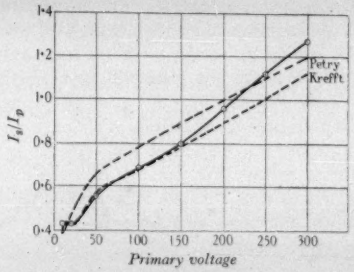

Figure 9. Secondary-emission coefficient for tungsten.

A similar curve, figure 10, for tantalum is in good agreement with the result obtained by Warnecke[4], by a method similar to that used by Petry.

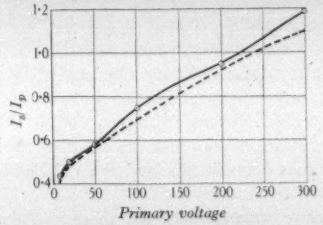

Figure 10. Secondary-emission coefficient for tantalum ——— author's results; – – – – Warnecke's results.

§ 8. THE EFFECT OF HIGH-VELOCITY SECONDARIES

In considering the method of obtaining the calibrating line for the primary current, we assumed that all secondaries, either from the anode or from the target, were emitted with zero velocity. We must now consider the effect of finite velocities of emission. If the secondaries all had a velocity low in relation to that of the primaries a straight line would still be obtained, although its range would be somewhat diminished. If, however, the secondaries had a range of velocities extending up to the primary velocity, these secondaries would begin to pass through the grid at different values of the abscissae, and a departure from linearity would result. If, however (and this is more nearly what happens) there were a number of low-velocity secondaries, which have no important effect, and also a number having very nearly the full primary velocity, these latter would always pass through the

grid. We must consider separately the secondaries leaving and arriving at the target. The number of those leaving the target would be proportional to the primary current. Such emission would reduce the slope of the line obtained when i_t is plotted against $\sqrt{(V_t/V_a)}$, but would not cause a departure from linearity. Straight lines corresponding to different values of V_t would, however, no longer be coincident, unless the proportion of such high-velocity secondaries were independent of primary voltage.

Of the secondaries leaving the anode, most will traverse the space within the grid and strike the anode again, but there will be a fraction which strike the target. The fraction thus collected by the target will decrease with increasing anode voltage, and it is possible that this fraction might be proportional to $\sqrt{(V_t/V_a)}$. But only in the case where the amount of high-velocity secondary emission is independent of primary voltage will a series of coincident straight lines be obtained for different values of V_t. Hence it is possible to obtain a straight line independent of V_t only if there is a high-velocity fraction of the secondaries which is independent of the primary voltage.

Let us now examine the experimental evidence with regard to high-velocity emission. Farnsworth[5] has found that for the metals nickel, copper, iron and silver, the full-velocity secondary emission, measured relatively to the primary current, ranges from 11 to 28 per cent at 10 V. and from 5 to 10 per cent at 50 V., while Haworth[6] found in the case of molybdenum that this ratio continues to fall from 50 to 125 V., being only 4 per cent of the total secondary emission (and therefore also about 4 per cent of the primary current) at the latter voltage. Hence the high-velocity secondary emission is not independent of voltage, and its effect should, therefore, be apparent in the curvature and non-coincidence of the calibrating lines taken with different target voltages. At the values of target voltage (100 to 300) used in the present work the errors would probably be from 2 to 4 per cent. The calibrating lines actually obtained are neither perfectly straight nor perfectly coincident, but the experimental errors of the readings are probably about 3 per cent, so that we cannot be sure that these irregularities are due to high-velocity emission. We may say that, to the degree of accuracy attained by the experiments, the effects of the initial velocities of the secondary electrons may be neglected.

§ 9. ACKNOWLEDGMENT

The author desires to tender his acknowledgment to the Marconiphone Company and the General Electric Company on whose behalf the work which has led to this publication was done.

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(6 Haworth, L. J. *Phys. Rev.* **48**, 88 (1935).

DISCUSSION

D. O. SPROULE. It is clear that in this method the electrons are incident on the filament at all possible angles. Hence the question of dependence of secondary emission on angle of incidence may be important. I recall having seen a report of an investigation of this factor, but do not remember the nature of the results. Could the author throw some light on this aspect of the problem, at least so far as it is relevant to this method?

Dr A. L. REIMANN. In considering the possible effects of the varying angles of incidence of the primary electrons on the results obtained by Mr Treloar, I think it should be borne in mind that, owing to the multicrystalline microstructure exhibited by the surfaces of heat-treated metals, the range of angles of incidence with crystal faces must be just as great in any experiment where a definite parallel beam of electrons is directed at any angle on to a macroscopically plane surface of a multi-crystalline specimen. In the case of such specimens, no important variation of secondary emission phenomena with apparent angle of incidence is to be expected.

AUTHOR'S reply. If the amount of secondary emission is dependent on the angle of incidence of the primary electrons, this factor will have to be taken into account in making use of this method of measurement. I have not been able to find any direct experimental evidence on this point for the case of multi-crystalline surfaces bombarded with slow electrons. It seems certain, however, that the primary electrons will be scattered through large angles by the metallic nuclei before losing most of their energy, so that any effect of their original direction is not likely to be very marked.

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THE THERMAL CONSTANTS OF SETTING CONCRETE

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ABSTRACT. The rise in temperature in a large mass of concrete during setting may be considerable, and the shrinkage stresses induced by the subsequent cooling may become large enough to cause cracking. It is, therefore, important to be able to calculate the rise of temperature likely to occur in such a mass. The calculation of the temperature-rise requires a knowledge of the thermal constants of the material. Hitherto no measurements have been made on concrete less than three days old, and the experiments made have mostly been on dry concrete. The values of the constants so obtained may differ considerably from those for fresh concrete. Methods have therefore been developed whereby measurements of the thermal conductivity and the thermal diffusivity of setting concrete can be made.

The thermal conductivity has been obtained by measuring the heat-flow between coaxial cylinders, and the diffusivity has been measured by means of observations on the rapid cooling of a cylindrical specimen. In both cases the effects of the heat evolved by the concrete have been eliminated by making experiments in a water bath controlled so that its rate of rise of temperature is the same as that produced in the concrete by the latter's own heat-evolution.

The accuracy of the methods has been tested by means of experiments on water. Good agreement is obtained with the results of Martin and Lang, which are probably the most reliable of previous data for water. Results are quoted for typical concrete specimens, and the values of the conductivity and the diffusivity obtained are compared with those for dry concrete.

§ 1. INTRODUCTION

In the designing of concrete structures it is frequently of importance to be able to estimate the temperature-rise which will be produced in a given mass of concrete by the heat evolved during setting. For this to be computed it is essential to know the size and shape of the mass and the nature of its surroundings, the thermal constants of the concrete, and its rate of evolution of heat at any time.

The methods of calculating from these data the temperature-rise for masses of concrete of various simple geometrical forms have been fully discussed by Fox[1, 2] and by Davey and Fox[3]. The mean values of the conductivity and diffusivity recommended by Davey and Fox are, however, open to some objection in that they are deduced from a consideration of experimental results on dry concrete at least three days old. It is known that the amount of moisture present in concrete has a considerable effect on the thermal conductivity, and since concrete during setting

is usually almost completely saturated with water, it might be expected to have a considerably higher conductivity than dry concrete. Furthermore, during the setting period some of the water combines with the cement, and the resulting decrease in the amount of free water present is likely to affect the values of the thermal conductivity and diffusivity of the concrete.

The object of the work described here has been to investigate these changes and to obtain more reliable mean values of the thermal constants of setting concrete for use in calculations of temperature-rise. Furthermore, a method has been developed at the Building Research Station for measuring the temperature-rise of concrete while this is setting under adiabatic conditions, and in order that the heat evolved may be calculated from this temperature-rise an accurate knowledge of the specific heat of the material is required.

Since the rate of the chemical reaction is affected appreciably by the temperature of the material, it is important to specify accurately the conditions of storage of the specimens during the setting period. Two simple methods of storage suggest themselves: (*a*) at constant temperature, and (*b*) under adiabatic conditions. In practice, more particularly in large masses of concrete, the conditions more nearly approximate to (*b*) than to (*a*). A further advantage of adiabatic storage is that it enables the effects of the heat evolved by the concrete to be eliminated easily from the experimental results. This method of storage has therefore been adopted.

The method of securing adiabatic conditions of storage for concrete specimens during setting has been fully described by Davey[4] and is only outlined briefly here. A specimen having the same constitution, and mixed at the same time as those to be studied, is enclosed in a vacuum flask which is immersed in a water bath. A thermocouple with one junction in the control specimen and the other in a glass tube immersed in the bath is connected to a sensitive relay system, which switches the immersion heaters in the bath on or off according as the temperature of the water is below or above that of the control specimen. Thus the temperature of the water never differs appreciably from that of the concrete, which is thereby prevented from exchanging heat with its surroundings. The accuracy with which the temperatures of the bath and the specimen can be made to agree depends on the sensitivity of the relay system. With the system used in the present work the two temperatures agreed at all times within $\frac{1}{10}^{\circ}$ C. The test specimens were stored in a bath controlled in this way, and by taking the temperature of the bath as the datum for all temperature measurements, the effects of the heat-evolution of the concrete were eliminated. Since the thermal constants are likely to be changing with time, small specimens were used so as to reduce the duration of the individual measurements.

The thermal conductivity k, and the thermal diffusivity h^2, were chosen for measurement as being most convenient. From these two quantities and the density ρ the specific heat s can be calculated if required, by means of the formula k, h^2 ρ, s

$$s = k/h^2\rho.$$

The methods of determining k and h^2 will be described separately.

§ 2. MEASUREMENT OF THERMAL CONDUCTIVITY

The thermal-conductivity measurements were made by the well-known method depending on the heat-flow between coaxial cylinders.

The specimens were cast in the annular space between two coaxial brass tubes *A* and *B*, figure 1, 20 cm. long and of radii 2·13 and 0·40 cm. respectively. The ends of the tube *A* were closed by rubber bungs in which holes were bored centrally to carry the tube *B*. A 40 s.w.g. constantan wire stretched down the centre of tube *B*

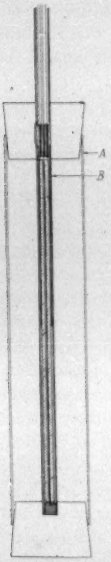

Figure 1. Longitudinal section of conductivity specimen.

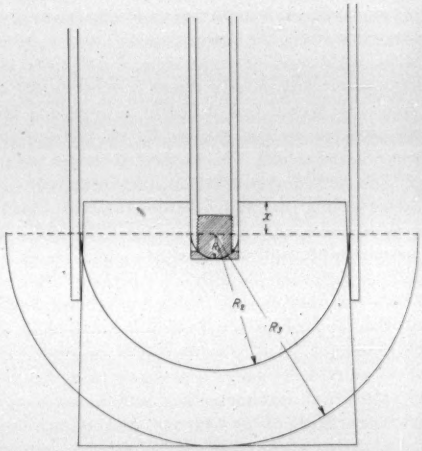

Figure 2.

formed the heating element. It was soldered at one end to a small brass plug which screwed into the bottom of the tube *B*. The other end of the heater wire was soldered to a 40 s.w.g. copper wire which passed out through a small hole in an ebonite plug at the upper end of the tube. The wires were silk-covered, and were further insulated by a coating of cellulose paint. A glass capillary tube which just fitted inside the inner brass tube surrounded the heater wire, the spaces between the glass and the wire and between the glass and the brass tube being filled with oil. In this way good thermal contact between the wire and the tube was secured, together with good electrical insulation. Another 40 s.w.g. copper wire was soldered to the upper end of tube *B* to provide the return lead for the current.

The temperature-difference between the two brass tubes was determined by means of 40 s.w.g. copper-constantan thermocouples soldered to the tubes. The wires forming the inner thermocouple passed down the inside of the tube *B*, and were soldered into small holes drilled diametrically opposite each other in the wall of the tube. These wires were insulated in the same way as the heater wire before they were soldered into position inside the tube. The outer thermocouple was soldered on to the outside of the tube *A*, the wires being protected from the water by several coats of cellulose paint. Owing to a large e.m.f., presumably of electrolytic origin, which was always present when the space between the tubes was filled with concrete, it was not possible to determine the temperature-difference directly by a single differential thermocouple. The two thermocouples accordingly had separate cold junctions which were placed in small glass tubes filled with paraffin and immersed in the water bath.

The e.m.fs. of the two thermocouples were read on a Tinsley thermocouple potentiometer. This instrument was calibrated directly in microvolts, and by observing galvanometer deflections readings could be made with an accuracy of a quarter of a microvolt. Since the difference between the two required e.m.fs. was of the order of 120 μV. it could be measured with an accuracy of 1 part in 400. The corresponding temperature-differences were read from a large-scale graph obtained with the aid of Beckmann thermometers. A current of about 0·8 A., supplied from a 12-volt battery, was passed through the heater wire, and maintained in the steady state a temperature-difference of about 3° C. between the two brass tubes.

With specimens of the dimensions given above, the steady state was reached in about 10 minutes after the switching on of the current. This steady state was, of course, only a steady state with respect to the controlled bath. Actually the whole specimen was rising in temperature at the same rate as the bath, but the heat required to maintain this rise was supplied by the concrete itself. Thus all the heat supplied to the heater, with the exception of certain small corrections to be discussed later, flowed out radially through the specimen, and the usual equation for heat-flow between coaxial cylinders could be applied, namely,

$$Q = 2\pi k\,(\theta_1 - \theta_2)/(\log_e R_2 - \log_e R_1) \qquad \text{.....(1),}$$

where Q is the radial heat-flow per unit length per second, θ_1, θ_2 are the temperatures of the inner and outer cylinders respectively, R_1, R_2 are the radii of the cylinders, and k is the thermal conductivity of the material. Q, θ_1, θ_2 R_1, R_2 k

The quantity of heat measured was the total quantity Q_0 supplied to the heater per second. Since the inner brass tube had a wall-thickness of about 0·1 cm., and must therefore have been practically at uniform temperature throughout its length, we can assume that the radial flow of heat was uniform over the whole length of the specimen. Q_0

Thus
$$Q \times l = Q_0 - 2H\,(\theta_1 - \theta_2) - C\frac{d\theta_0}{d\tau} \qquad \text{.....(2),}$$

where l is the length of the specimen, H is the heat-loss from one end of the specimen for unit difference of temperature between the inner and outer cylinders, C is the l, H C

θ_0, τ heat capacity of the inner brass tube and its contents, and $d\theta_0/d\tau$ is the rate of rise of temperature of the controlled bath during the experiment.

The quantity H cannot be calculated exactly owing to the shape of the rubber bungs closing the ends of the tube. Being small, however, compared with Q_0, it can be estimated with sufficient accuracy by the method adopted below.

A longitudinal section of the lower end of the specimen is shown in figure 2. The heat-loss through the bung may be regarded as made up of two parts: (1) the x loss between concentric cylinders of radii R_1 and R_2 and length x, and (2) the loss R_3 between concentric hemispheres of radii R_1 and R_2, or R_1 and R_3. If we take R_1 and R_2 for the radii of the hemispheres, the loss obtained will certainly be greater than that actually occurring, while if we take R_1 and R_3, the calculated loss will probably be too small. The two values thus obtained do not differ very widely, and their mean may be taken as sufficiently accurate for our purpose.

The values of R_1, R_2 and R_3 were respectively 0·40, 2·13, and 2·50 cm., while x measured 0·6 cm. Taking k for rubber as $0{\cdot}45 \times 10^{-3}$, we thus obtain for the cylindrical loss

$$H = 2\pi kx/(\log_e R_2 - \log_e R_1)$$
$$= 0{\cdot}0008 \text{ cal. per sec. per °C. temperature-difference,}$$

and for the hemispherical loss

$$H_s < 2\pi kR_1R_2/(R_2 - R_1)$$
$$< 0{\cdot}0014 \text{ cal. per sec. per °C. temperature-difference,}$$

and
$$H_s > 2\pi kR_1R_3/(R_3 - R_1)$$
$$> 0{\cdot}0013 \text{ cal. per sec. per °C. temperature-difference.}$$

Thus H lies between 0·0022 and 0·0021 cal. per sec. per °C. temperature-difference between the tubes, or, taking the mean value,

$$H = 0{\cdot}00215 \text{ cal. per sec. per °C.}$$

Assuming a similar loss at the upper end of the specimen, we have finally

$$2H = 0{\cdot}0043 \text{ cal. per sec. per °C.}$$

The total heat-input, Q_0, necessary to maintain a temperature-difference of 3° C. between the tubes was of the order of 1·3 cal. per sec., so that the heat-loss from the ends is only about 1 per cent of the total input. The error involved by using the above approximate calculation of end losses will thus be negligible.

The third term on the right of equation (2) represents the heat required to produce in the inner brass tube and its contents a temperature-rise exactly similar C to that of the controlled bath. The thermal capacity C of the tube and its contents could be calculated from the specific heats and masses of the separate constituents and was approximately equal to 2 cal. per °C. Since the rate of rise of temperature of the bath never exceeded 2° C. per hour during an experiment, and was usually less than 1° C. per hour, this term cannot account for more than one-tenth of 1 per cent of the total heat-input, and it has accordingly been neglected.

A further small error may arise from the fact that the rate of heat-evolution of the concrete depends on its temperature. During an experiment the centre of the

conductivity specimen is raised in temperature above the controlled bath, and will thus be evolving heat more rapidly than when the specimen is unheated. Thus more heat will be produced by the concrete than is necessary to maintain the correct rate of rise of temperature in the specimen, and the excess heat will be added to the radial flow. But since the temperature-excess at the centre is only about 3° C., and since, moreover, owing to the logarithmic decrease of temperature with radius, only a very small part of the concrete is seriously affected, this error may also be neglected.

The possibility of error in the thermal-conductivity experiments due to the two cylinders not being accurately coaxial is discussed in the Appendix, where it is shown that the error from this cause is not likely to exceed one-half of 1 per cent. The thermal-conductivity measurements will therefore be in error by an amount not exceeding 1 per cent.

§ 3. MEASUREMENT OF THERMAL DIFFUSIVITY

Consider a cylinder of radius R supposed infinite in length, and having an initial temperature-distribution given by R

$$\theta = f(r). \qquad \theta, f, r$$

Suppose that the cylinder is placed, at time τ equal to 0, in surroundings at zero temperature, and that the rate of heat-loss from the surface is proportional to the difference of temperature between the surface and the surroundings. τ

The equation of heat-flow in the cylinder is

$$\frac{\partial\theta}{\partial\tau} = h^2\left(\frac{\partial^2\theta}{\partial r^2} + \frac{1}{r}\frac{\partial\theta}{\partial r}\right) \qquad \text{.....(3)}, \qquad h$$

and the boundary conditions to be satisfied are

$$\theta = f(r) \quad \text{at} \quad \tau = 0 \qquad \text{.....(4)}$$

and

$$-k\frac{\partial\theta}{\partial r} = E\theta \quad \text{at} \quad r = R \qquad \text{.....(5)},$$

where E is the amount of heat lost per cm.^{2} per sec. from the surface for unit difference of temperature between the surface and the surroundings. E

It can then be shown[5] that the temperature at any point in the cylinder at time τ is given by the equation

$$\theta = \sum_1^\infty A_n J_0(\alpha_n r)\, e^{-\alpha_n^2 h^2 \tau} \qquad \text{.....(6)},$$

where A_n, α_n are constants. A_n, α_n

But the values of $\alpha_1, \alpha_2, \ldots$ form an increasing series, and thus for large values of τ the higher terms of the series represented by equation (6) will be small compared with the first. Thus for sufficiently large values of τ we can neglect all terms except the first and the solution becomes

$$\theta = A_1 J_0(\alpha_1 r)\, e^{-\alpha_1^2 h^2 \tau}.$$

For concrete specimens of the dimensions used in the present tests, this simplification was permissible at values of τ greater than 120 sec. Hence if θ_1

is the temperature at some point inside the cylinder at time τ_1, and θ_2 is the temperature at the same point at a later time τ_2, we have

$$\frac{\theta_1}{\theta_2} = e^{-\alpha_1^2 h^2 (\tau_1 - \tau_2)},$$

i.e.
$$h^2 = (\log_e \theta_1 - \log_e \theta_2)/\alpha_1^2 (\tau_2 - \tau_1) \qquad \text{.....(7).}$$

θ_0, θ_R Also, if θ_0 and θ_R are the temperatures at the axis and surface of the cylinder respectively at the same time, we have

$$\theta_0/\theta_R = J_0(0)/J_0(\alpha_1 R) = 1/J_0(\alpha_1 R),$$

i.e.
$$J_0(\alpha_1 R) = \theta_R/\theta_0 \qquad \text{.....(8).}$$

Since equations (7) and (8) involve only ratios of temperatures, it is sufficient to measure quantities which are proportional to temperatures. Equation (8) then serves to determine α_1, and h^2 can be calculated from equation (7).

Experimental procedure. The measurements of diffusivity were made with specimens identical with those used for the conductivity determinations, except that they had a single copper-constantan thermojunction of 40 s.w.g. wire at the centre instead of the inner brass tube.

The specimen was kept in the controlled bath until a measurement of the diffusivity was to be made, when it was removed and placed for a few minutes in a bath at a temperature about 10° C. lower than that of the controlled bath. During this period, if it be assumed that the cooling was entirely radial, the specimen acquired a temperature-distribution of the form $\theta = f(r)$.

The specimen was then quickly replaced in the controlled bath, and after a period of about 2 min. readings of the deflections of a Zeiss loop galvanometer were commenced with the instrument connected alternately to the axial and surface thermocouples by means of a mercury switch. The readings were continued at intervals of 10 sec. until the deflections became too small to be read accurately. The galvanometer was known to have a linear {current, deflection} characteristic. Since, moreover, a full-scale deflection was produced by a temperature-difference of about 3° C., it can be assumed without appreciable error that its deflections were proportional to the temperature-difference being measured.

The logarithms to base 10 of the readings thus obtained were plotted against time. If all the conditions of the theory were fulfilled, this gave two parallel straight lines whose slope determined

$$(\log_{10} \theta_1 - \log_{10} \theta_2)/(\tau_2 - \tau_1);$$

h^2 was then calculated from the equation

$$h^2 = 2{\cdot}303\ (\log_{10} \theta_1 - \log_{10} \theta_2)/\alpha_1^2 (\tau_2 - \tau_1).$$

α_1 being determined from equation (8) in the manner indicated above. A small error may arise in the determination of α_1 if the central thermocouple is not exactly on the axis of the cylinder. Fortunately a relatively large error in the position of this thermocouple only involves a small error in the value of α_1. The possible magnitude of the error can be estimated as follows. Suppose that the central

thermocouple is as much as 2 mm. from the axis, which it is unlikely to be. For cylinders of the dimensions used the value of α_1 is approximately unity, so that, instead of

$$\theta_R/\theta_0 \text{ or } J_0(\alpha_1 R),$$

the quantity actually measured would be

$$J_0(\alpha_1 R)/J_0(\alpha_1 \times 0{\cdot}2) \text{ or } J_0(\alpha_1 R)/0{\cdot}99.$$

The error in the estimation of $J_0(\alpha_1 R)$ would thus be of the order of 1 per cent. But for the values of $(\alpha_1 R)$ with which we are concerned, namely about 2, a change of 3 per cent in the value of $J_0(\alpha_1 R)$ is caused by a variation of only one-half of 1 per cent in the value of $(\alpha_1 R)$. The value of α_1 deduced would thus be in error by about one-sixth of 1 per cent if the central thermocouple were as much as 2 mm. from the axis. This source of error has therefore been neglected.

It was assumed that there was no longitudinal flow of heat. The cylinders had a length approximately ten times their radius, and were insulated at the ends by rubber bungs, so that any longitudinal heat-flow must have been small. That it had no appreciable effect on the values of h^2 is shown by the results for water quoted below.

A small error must also be caused by the variation of the rate of heat-evolution of the concrete with temperature. If this error had been appreciable, there would have been a departure from linearity in the relation between τ and $(\log \theta_1 - \log \theta_2)$. This was not observed, and the error was accordingly neglected.

§ 4. TEST OF THE METHODS

The choice of a suitable standard material with which to test the apparatus presented some difficulty. Such a material should have at least one of its thermal constants accurately known, should be readily obtainable in a pure state, and should be without crystalline structure. No satisfactory solid substance having all these properties could be found. It was therefore decided to make a series of experiments with water.

The apparatus as described is not suitable for measurements on liquids, owing to the transfer of heat by convection. This difficulty was overcome by filling the tubes with a mixture of cotton wool and water. The presence of the cotton wool prevented convection, and had very little effect on the thermal constants of the mixture. Moreover its effect could easily be allowed for by making experiments with various densities of cotton-wool packing, and by extrapolating from the results obtained. In this way the thermal conductivity and diffusivity of water have been measured over the range of temperature from 20 to 50° C.

The experiments were made with distilled water, boiled immediately before use to expel any dissolved air, and with three different densities of packing of the cotton wool. The tubes were first filled with water, and the cotton wool was then added in small pieces and rammed down to the required density with a glass rod. It was found that by this procedure the specimens could be obtained free from entrapped air bubbles much more easily than by first packing the tube with the

cotton wool and then adding the water. The results are shown graphically in figures 3 and 4.

The present results for the conductivity can best be represented by the formula

$$k \times 10^3 = 1{\cdot}39_2\,(1 + 0{\cdot}0023t).$$

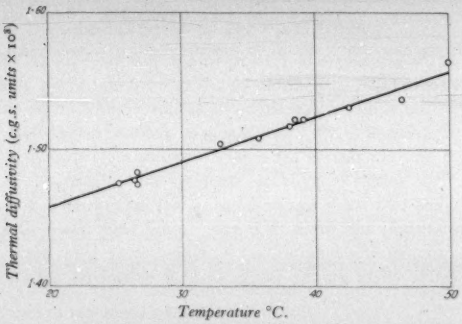

Figure 3. Thermal diffusivity of water.

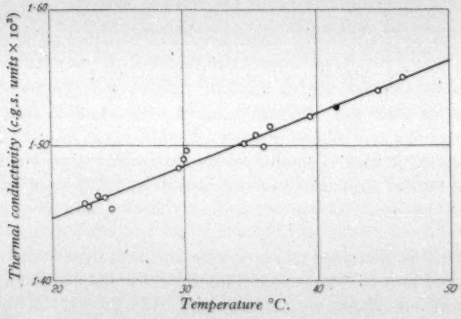

Figure 4. Thermal conductivity of water.

This is in excellent agreement with the results of Martin and Lang[6], who found

$$k \times 10^3 = 1{\cdot}39_4\,(1 + 0{\cdot}0023t).$$

Earlier measurements of the conductivity of water, which have been summarized in a table given by Martin and Lang, show a considerable divergence both in the value of k at 0° C. and in the temperature coefficient.

No previous direct measurements of the diffusivity of water appear to have been made. Since, however, both the specific heat and the density of water are accurately known, a comparison can be made between the values obtained for the diffusivity and those obtained for the conductivity.

At 20° C. the density of water is 0·998 and the specific heat is 1·000, while the corresponding values at 50° C. are 0·988 and 0·999. Thus at 20° C. we should find $k/h^2 = 0{\cdot}988$, and at 50° C. $k/h^2 = 0{\cdot}987$. Taking the mean values at 20° and 50° C. from figures 3 and 4, we find $k/h^2 = 1{\cdot}008$ at 20° C., and $k/h^2 = 0{\cdot}997$ at 50° C. Both these values are too large by about 1 per cent and it thus seems probable that the values of diffusivity are too low by this amount. This error cannot be caused by longitudinal heat-flow in the diffusivity specimens, since this would increase the rate of change of temperature and thus give a high value for h^2. The error probably arises from the assumption of a linear relation between the diffusivity and the amount of cotton wool in the tube. This source of error will not arise in experiments with concrete, and it is therefore probable that both the conductivity and the diffusivity experiments give results which are correct to within 1 per cent.

§ 5. EXPERIMENTS ON CONCRETE

In the experiments on concrete there were certain points which required special attention. The measurements, as has already been stated, were made in the controlled bath and the temperature fluctuations of this bath caused by the operation of the relay, although small, were of sufficient magnitude to be appreciable in comparison with the temperature-differences which were being measured. It was therefore found desirable to suspend the operation of the automatic control while an experiment was being performed, and to adjust the heat-input to the bath by means of rheostats in the heater circuit, so that the correct rate of rise of temperature of the bath was maintained. For purposes of indication the thermocouple normally connected to the sensitive relay was connected instead to a mirror galvanometer, the deflection of which remained constant at or near zero when the correct rate of rise of temperature was achieved. By this method the rates of rise of temperature of the bath and of the controlling specimen could be made to agree very closely.

This suspension of the automatic control, although quite satisfactory as far as the thermal-conductivity experiments were concerned, introduced a further source of error into the diffusivity measurements. The diffusivity specimen, when replaced in the controlled bath after being cooled, caused a slight cooling of the bath, and consequently the temperatures of the specimen and the bath approached each other more rapidly than would have been the case if the bath-temperature had been unaffected by the introduction of the specimen, as it is assumed to be in the theory. Owing to the very short time available in the diffusivity experiments, it was not possible to compensate for this effect by alteration of the heat-input, and it was therefore necessary to correct the observed values of diffusivity.

It may reasonably be supposed that the error arising from this cause will be proportional to the ratio of the rate of change of the temperature of the bath to that of the test specimen. Thus if the change of deflection of the mirror galvanometer connected to the tank thermocouple during the course of an experiment be δd, and the corresponding change of deflection of the Zeiss galvanometer connected to the central thermocouple of the test specimen be δD, the error in the result will be

proportional to $\delta d/\delta D$. The constant of proportionality was determined by making two experiments with the same specimen but with slightly different rates of heat-input to the tank, i.e. with different values of $\delta d/\delta D$. From the two apparent values of h^2 thus obtained it was found that a value of $\delta d/\delta D$ equal to 0·01 caused an error of 1·4 per cent in the diffusivity. In all subsequent experiments the value of $\delta d/\delta D$ was observed, and a proportionate correction was applied to the results. Since this was usually of the order of 1 per cent, and never exceeded 2 per cent, the final results cannot be seriously in error. A typical set of readings for a diffusivity experiment on a concrete specimen is given in table 1.

Table 1

Time (sec.)	Axial thermocouple		Surface thermocouple	
	Deflection D_1	$\log_{10} D_1$	Deflection D_2	$\log_{10} D_2$
0	86·4	1·9365	—	—
10	—	—	6·9	0·8388
20	67·7	1·8306	—	—
30	—	—	5·3	0·7243
40	52·5	1·7202	—	—
50	—	—	3·9	0·5911
60	40·5	1·6075	—	—
70	—	—	3·1	0·4914
80	31·2	1·4942	—	—
90	—	—	2·5	0·3979
100	24·1	1·3820	—	—
110	—	—	1·9	0·2788
120	18·8	1·2724	—	—
130	—	—	1·5	0·1761
140	14·5	1·1614	—	—
150	—	—	1·1	0·0414
160	11·4	1·0569	—	—

In figure 5 the values of $\log_{10} D_1$ and $\log_{10} D_2$ are plotted against time. It will be seen that two parallel straight lines are obtained; this shows that the conditions of the theory are fulfilled.

From figure 5 we obtain

$$\log_{10} \theta_t - \log_{10} \theta_{t+180} = 1{\cdot}00$$

and $$\log_{10} J_0(\alpha_1 R) = \bar{2}{\cdot}944,$$

i.e. $$J_0(\alpha_1 R) = 0{\cdot}0879,$$

whence $$\alpha_1 R = 2{\cdot}241.$$

Therefore, since $R = 2{\cdot}13$ cm. we have

$$h^2 = 0{\cdot}0115_6.$$

This is the apparent value of h^2 uncorrected for temperature-changes in the tank during an experiment. In this experiment $\delta d/\delta D$ was equal to 0·013.

Hence the true value of h^2 is

$$0{\cdot}0115_6/(1{\cdot}014 \times 1{\cdot}013) \text{ or } 0{\cdot}0113_6.$$

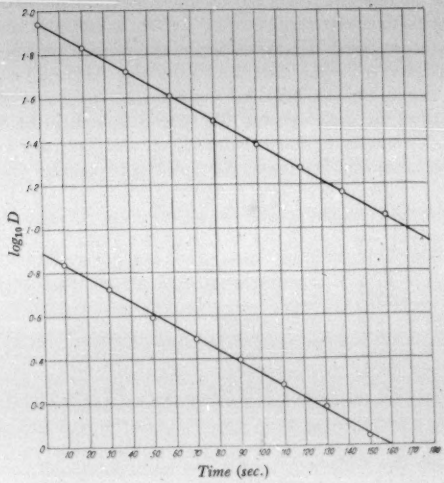

Figure 5.

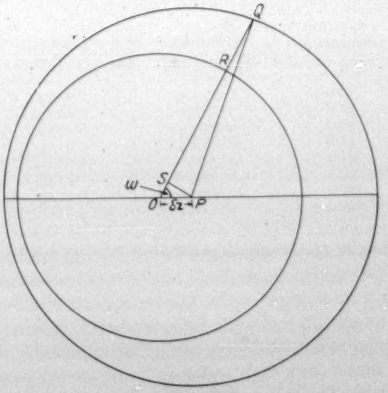

Figure 6.

The thermal constants of concrete will of course be influenced by a number of factors, such as the type and size of the aggregate used, the proportions of the mix, and the density of the concrete. Up to the present no attempt has been made to study these factors in detail, the preliminary experiments having been restricted to a siliceous aggregate, to normal and rapid-hardening Portland cements, and to a standard mix, namely cement, sand and water in the proportions of 1 : 6 : 0·6 by weight. In view of the dimensions of the specimens a small aggregate has been used, the particles ranging in size between $\frac{1}{100}$ in. and $\frac{1}{8}$ in., and being uniformly graded within these limits. The results for typical specimens are shown in tables 2 and 3.

Table 2. Normal Portland cement concrete. Density 2·11

Time after mixing (hours)	Tank-temperature (°C.)	Conductivity k	Diffusivity h^2	Specific heat s
4	18·6	0·00578	$0{\cdot}0110_4$	0·248
$6\frac{1}{2}$	19·8	0·00578	$0{\cdot}0110_7$	0·247
25	33·0	0·00573	$0{\cdot}0110_9$	0·245
31	35·1	0·00575	$0{\cdot}0110_9$	0·246
$48\frac{1}{2}$	40·0	0·00581	$0{\cdot}0112_5$	0·245
55	41·1	0·00582	$0{\cdot}0112_4$	0·245
72	43·3	0·00586	$0{\cdot}0113_5$	0·244

It will be seen that with both normal and rapid-hardening Portland cements the thermal conductivity and diffusivity increase slightly with time, while the specific heat shows a slight decrease.

Table 3. Rapid-hardening Portland cement concrete. Density 2·13

Time after mixing (hours)	Tank-temperature (°C.)	Conductivity k	Diffusivity h^2	Specific heat s
$4\frac{1}{2}$	20·9	0·00594	$0{\cdot}0112_5$	0·248
7	22·3	0·00595	$0{\cdot}0113_0$	0·247
13	30·0	0·00599	$0{\cdot}0113_1$	0·248
$24\frac{1}{2}$	38·6	0·00603	$0{\cdot}0114_5$	0·247
31	41·4	0·00606	$0{\cdot}0115_7$	0·246
$48\frac{1}{2}$	45·6	0·00608	$0{\cdot}0116_8$	0·245
55	47·0	0·00617	$0{\cdot}0117_8$	0·246
72	49·1	0·00622	$0{\cdot}0118_8$	0·246

The mean values of conductivity and diffusivity recommended by Davey and Fox, on the basis of a study of the work of a number of investigators, are 0·0045 c.g.s. units and 0·009 c.g.s. units respectively. The results now obtained are considerably higher than these values. The present results, moreover, show no sign of decreasing with time to the mean values for dry concrete. This is probably due to the fact that the specimens are almost completely sealed up inside the tubes, and there is no way of escape for moisture. The excess water which does not combine with the cement thus remains behind, keeping the concrete moist and consequently increasing the conductivity.

In this respect the present technique again imitates fairly closely the natural conditions, for during the setting period, when the shuttering is still in position and the surface of the concrete is usually covered, the loss of water by evaporation from a mass of dense concrete must be extremely small.

It is hoped to continue these experiments in order to find how the values of the thermal constants are affected by the other factors mentioned above. The variation is, however, expected to be small, and, in view of the approximate nature of the calculations of temperature-rise for which the constants are required, it is suggested that for the time being the values 0·006 c.g.s. units for the conductivity and 0·115 c.g.s. units for the diffusivity should be adopted. Certainly these values will be more accurate than those previously assumed. As regards the specific heat, the mean value obtained from the experimental results is 0·246. The value computed from the specific heats of the separate constituents of the concrete is 0·25, and it is therefore recommended that the value 0·25 be used.

§6. ACKNOWLEDGMENTS

In conclusion, the author wishes to express his thanks to Mr H. E. Beckett for much valuable advice and encouragement during the course of the work, and to the Director of Building Research, for permission to publish this paper.

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APPENDIX

HEAT-FLOW BETWEEN NON-COAXIAL CYLINDERS

Since it was difficult in practice to ensure that the two cylinders used in the conductivity experiments should be accurately coaxial, an approximate calculation of the error likely to be introduced by this assumption has been made.

Let R_1 and R_2 be the radii of the inner and outer cylinders respectively, and Z the distance apart of their axes, which are assumed parallel. If Z is small we can assume that the isothermal surfaces are cylinders, and that the radius r of any isothermal cylinder is connected with the distance z of its axis from that of the inner cylinder by the equation

R_1, R_2, Z r z

$$z=(r-R_1)\,Z/(R_2-R_1) \qquad \text{.....(10).}$$

Consider a shell bounded by the isothermal cylinders whose radii are r and $r+\delta r$, and whose axes are distant z and $z+\delta z$ from that of the inner cylinder.

t, ω The thickness t of the shell in a direction making an angle ω with the line of centres will be, to the first order in δr,

$$\delta r \{1 + Z \cos \omega/(R_2 - R_1)\}.$$

$\delta\theta$ If $\delta\theta$ is the temperature-difference across the shell and k the conductivity of the δQ material, the heat-flow δQ per unit area across the shell in the direction ω is thus

$$-k\delta\theta/\delta r \{1 + Z \cos \omega/(R_2 - R_1)\}.$$

Q Integrating for all angles of ω we find that the total heat-flow Q through the shell per unit length is given by

$$Q = -2\int_0^{\pi} \frac{k.\delta\theta.r}{\delta r \{1 + Z \cos \omega/(R_2 - R_1)\}} . d\omega$$

$$= -\frac{2k(R_2 - R_1) r\delta\theta}{\delta r} \int_0^{\pi} \frac{d\omega}{Z \cos \omega + R_2 - R_1}$$

$$= -\frac{2\pi k (R_2 - R_1) r\delta\theta}{\sqrt{\{(R_2 - R_1)^2 - Z^2\}}\, \delta r}.$$

Since Q is independent of r, we can write

$$Q\frac{\delta r}{r} = -\frac{2\pi k (R_2 - R_1)}{\sqrt{\{(R_2 - R_1)^2 - Z^2\}}} . \delta\theta,$$

which, on integration from R_1 to R_2, gives

$$Q = \frac{2\pi k (\theta_1 - \theta_2)}{\log_e R_2 - \log_e R_1} . \frac{R_2 - R_1}{\sqrt{\{(R_2 - R_1)^2 - Z^2\}}}.$$

This expression differs from that for coaxial cylinders only in the factor

$$\frac{R_2 - R_1}{\sqrt{\{(R_2 - R_1)^2 - Z^2\}}}.$$

With a value for Z of 0·2 cm.—which is greater than is likely to occur in practice—and with R_1 equal to 0·396 cm. and R_2 to 2·13 cm., this factor is equal to 1·007.

Thus the error in the conductivity measurements due to the two cylinders not being coaxial is not likely to exceed one-half per cent.*

* Since this paper was written it has been pointed out by Dr F. Garwood, of the Building Research Station, that the exact expression for the heat-flow between non-coaxial cylinders is

$$Q = 2\pi k (\theta_1 - \theta_2) / \log_e . \frac{R_1 [R_2^2 - R_1^2 + Z^2 - \sqrt{\{(R_2^2 - R_1^2 + Z^2)^2 - 4R_2^2 Z^2\}}]}{R_2 [R_2^2 - R_1^2 - Z^2 - \sqrt{\{(R_2^2 - R_1^2 + Z^2)^2 - 4R_2^2 Z^2\}}]}.$$

According to this formula, the error when $Z = 0{\cdot}2$ cm. is 0·5 per cent, and this is in substantial agreement with the value of 0·7 per cent given by the approximate method.

535·337:546·291

ELECTRON ENERGIES AND EXCITATION IN THE HELIUM POSITIVE COLUMN

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ABSTRACT. The results of previous experimental investigations of the intensities of the spectral lines emitted from helium discharges are discussed, and a distribution function for the energies of the electrons is suggested in order to account for these results. The variation of the intensities of the lines with the pressure of the gas is then calculated, and curves are drawn representing the relative intensities of the various lines at different pressures. These curves are compared with those representing the observed variations of the intensities. The general agreement between the two sets of curves supports the conclusion that the distribution of the energies of the electrons in helium is of the form suggested. In this case the distribution may be expressed approximately by the formula

$$dN/N = (Ae^{-3y/2} + e^{-0\cdot 4y^2})\, y^{\frac{1}{2}}\, dy,$$

where N is the total number of electrons of mean energy E_1, dN is the number with energies lying between E and $E+dE$, A is a constant of the order of 5×10^{-3}, and y is E/E_1.

It is then concluded that the distribution of the energies of the vast majority of the electrons in the helium positive column is determined by the process of diffusion and the mean loss of energy in elastic collisions with atoms of the gas; but that a small fraction 2×10^{-3} of the total number form a group with their energies distributed according to Maxwell's formula corresponding to the same mean energy. It is pointed out that this small group of electrons is of predominating influence in the helium discharge at high pressures as far as excitation and ionization are concerned.

§ 1. INTRODUCTION

In recent years there have been many investigations[1, 2, 3] of the variations of the intensity of the light emitted from the positive column of the helium discharge when the pressure of the gas is altered. These experiments have been carried out with both high-frequency and direct-current discharges in wide tubes, and they have been chiefly confined to the visible spectrum. Various methods of measuring the intensity of the light emitted have been adopted; for example, colour filters have been used in conjunction with photoelectric or selenium cells, and also the spectra have been photographed. There is good agreement between the results of all the experiments. The intensities of the lines were found to be directly proportional to the current, and to increase as the pressure of the gas was decreased from 40 mm. to about 0·5 mm. while the current was maintained constant. However, the most notable feature is the very rapid increase of intensity with pressure in the neighbourhood of 1 mm.

The general explanation of these results has been given previously[1,2,3], but the theory may be explained briefly in the following way.

E_1 When a stream of electrons moves through a gas in a uniform electric field their mean energy of agitation E_1 may be expressed as a simple function of the ratio of Z, p the intensity of the electric force Z to the pressure p of the gas if E_1 is primarily determined[4]* by the energy losses in elastic collisions with the atoms of the gas. The mean energy has been determined accurately by means of experiments on the lateral diffusion of a stream of electrons, and for a range of values of Z/p from about 1 to 2 the value of E_1 is almost exactly $2Z/p$ for helium when Z is expressed in volts per centimetre and p in millimetres. Thus the mean energies of the electrons in the uniform positive column at various pressures can be found by determining the ratios Z/p for those pressures. Further, it follows from Townsend's theory that the same processes obtain in the high-frequency luminous glow, and E_1 is also given for h.f. discharges when Z is the r.m.s. value of the force.

V Now the excitation energy V of the various lines in the helium spectrum is of the order of 22 V., and this is much greater than the mean energies which lie between 2 and 6 V. Thus it follows that the energies of the electrons are distributed about the mean energy, so that only a small fraction of the total number of electrons have energies greater than V. Hence a small change in the value of E_1 causes a large change in the number of electrons with energies greater than V, which are capable of exciting the atoms of the gas. For example, the value of the mean energy is only doubled when the pressure is reduced from 40 mm. to about 0·5 mm., but the number of electrons with energies greater than V is increased about a thousand times. This results in a great increase in the intensity of the light at the lower pressures for a given current.

It is the purpose of this paper to suggest a distribution formula for the energies of the electrons in helium, and then to show how the observed variation of the intensity of the lines in the visible spectrum with the pressure of the gas in the discharge tube may be accounted for throughout the whole range of pressures investigated experimentally. The relative intensities of the most prominent lines have been measured accurately by Keyston by a spectrophotographic method at different pressures between 40 mm. and 0·32 mm., and these results will be compared with the relative intensities of the lines deduced theoretically.

§ 2. THE EXPERIMENTAL DATA

The intensities of the various lines measured by Keyston and published in his paper[3] are given again, for purposes of comparison, in table 1 in which the intensity of the lines when the gas pressure is 7 mm. is in each case taken to be 100. These measurements are in good agreement with those found in the earlier investigations, when photoelectric cells and colour filters were used, throughout the

* The function depends on the mean free path L of the electrons in the gas at 1 mm. pressure, the average loss of energy λ in an elastic collision, and the distribution of the energies of the electrons about the mean. When all the energies are equal (1) $E_1 = L/\sqrt{(3\lambda)}.Z/p$; and for a Maxwellian distribution $E_1 = L/\sqrt{(2{\cdot}66\lambda)}.Z/p$.

range of pressures from 40 mm. to about 4 mm. At pressures of about 0·5 mm. it is not easy to measure the electric force in the positive column accurately, and the values of Z/p (and consequently of E_1) for the pressures 0·78 and 0·32 which are given in the original table were there considered to be only approximate determinations. Now in the following calculations of the intensities of the lines it is very important to know the exact values of the mean energies of the electrons at these two pressures, and since the values of Z/p are not known they may be found by extrapolation.*

These estimated values of E_1, together with the corresponding values of W_1, the drift velocity[15] of the electrons, are as follows: W_1

$p=0{\cdot}78$, $E_1=5{\cdot}06$ V., $W_1=1{\cdot}7\,.\,10^6$ cm./sec.
$p=0{\cdot}32$, $E_1=5{\cdot}8$ V., $W_1=2{\cdot}45\,.\,10^6$ cm./sec.

§ 3. THE DISTRIBUTION FORMULA

The distribution of the energies of electrons in a gas under a uniform electric field is determined by processes, such as diffusion, which are different from those which set up the Maxwellian distribution. For very small values of the electric field, when the electrons are in thermal equilibrium with the gas atoms, the energy-distribution is Maxwellian; but when the mean energy increases, as a result of an increase in the electric force, the distribution changes continuously from the Maxwellian form to one which is determined by the process of diffusion. Formulae representing such a distribution have been given previously by Townsend, Druyvesteyn and others[5,6,8,9], and the manner in which the distribution changes from the Maxwellian form with very weak fields to the diffusion form when the mean energy is of the order of 100 times that of the gas atoms has also been pointed out by Townsend[7]. This distribution may be expressed in the form

$$dN_1 = N_1 y^{\frac{1}{2}} e^{-0{\cdot}55y^2}\, dy \qquad \ldots\ldots(1), \qquad N_1$$

where $y=E_x/E_1$, and N_1 is the total number of electrons with the mean energy y E_1, and dN_1 is the number with energies lying between E_x and E_x+dE_x. E_x

This expression is obtained on the following assumptions. (i) That the mean free path L of the electrons in the gas at 1 mm. pressure is a constant, and independent of the energy E_x of the electrons; (ii) that the loss of energy by an electron in an elastic collision with an atom of the gas may be expressed as a constant fraction L λ of the energy of the electrons, and that there are no collisions except of this kind— λ i.e. the losses of energy in large amounts, such as would be required for excitation and ionization may be neglected; and (iii) that the mean energy of agitation of the electrons is large compared with that of the gas atoms.

* If the observed intensities of the various lines are plotted against the values of E_1 originally given the graphs are nearly straight lines, but they all show a sudden change of direction at a value of E_1 of about 4·7 V. By extrapolating the straight sections for greater values of E_1 the corrected values of the mean energy corresponding to the observed intensities may be found. These estimates may be checked by plotting various functions of E_1, which are encountered below, against the pressure, and then extrapolating to the pressure 0·78 mm. and 0·32. The values of the functions at these points then determine E_1.

For low values of Z/p such as those obtained in the positive column in helium and neon in wide tubes these conditions are sensibly fulfilled, and the distribution expressed in equation (1) has been applied in researches on the excitation of helium and neon in discharges[1, 2, 3]. However, it was found that the observed rate of variation of the intensity of the light with pressure could not be accounted for by assuming this distribution formula for the electrons. A formula which gave a wider distribution was found necessary. On the other hand, the assumption of a Maxwellian distribution gave better agreement than the diffusion formula throughout the limited range of pressures investigated in these experiments, when the mean energy of agitation was less than 4 V. Further, under the same conditions, a Maxwellian distribution was able to account for the observed rate of variation of the electric force with the gas pressure in the positive column in helium[10]. Now it was emphasized in that case that it is only to those electrons which have energies very much larger than the mean that Maxwell's formula need apply, and the energies of the electrons more nearly equal to the mean may be distributed in an entirely different way. Further, it is only a small fraction of the total number of electrons that have the high energies necessary to excite or ionize the atoms of the gas, so that it is only a small fraction of the total number of electrons that must be distributed according to Maxwell's formula in order to account for the experimental results. On the other hand, the results of Keyston show that the suitability of Maxwell's formula breaks down completely at low pressures less than 4 mm., i.e. with mean energies greater than about 4 V. In deducing the diffusion expression

m (i) the mean loss of energy of an electron of mass m in a collision with an atom of
M mass M is assumed to be a constant fraction λ of the energy E_x, and the variations of λ about the mean are neglected. Now when the ratio Z/p is low the coefficient λ is not a constant $2m/M$ but is more nearly represented by $(1 - E_1/E_0).2m/M$, where E_0 is the mean energy of the gas atoms. This has been confirmed by the results of Townsend and Bailey on the motions of electrons in gases, and it shows that the effect of the energy of the gas atoms in collisions with electrons may not be neglected when Z/p is low, i.e. at high pressures. However, this variation of the energy loss about the mean loss may be regarded as the mechanism which sets up a Maxwellian distribution, and the lower the mean energy of the electrons the more important does this mechanism become. It is significant that at the higher pressures, when the mean energy of the electrons is low, the Maxwellian distribution is able to account for the observed changes both of light intensity and of electric force with the pressure of the gas. Again, collisions among the electrons themselves tend to set up a Maxwellian distribution of their energies.

Only experiments performed with comparatively high mean energies of the electrons, i.e. with pressures less than 1 mm., will enable the distribution of the energies of the main body of electrons to be found by these methods. For with high pressures, and consequently low mean energies, the excitation energies are about 6 or 8 times the mean energy, but with pressures of about 1 mm. the energies of the exciting electron are only about 3 or 4 times the mean. Consequently the number of electrons concerned in excitation or ionization is very much greater at

the lower pressures than at high pressures. If the distribution formula were known it would be possible, by making reasonable assumptions as to the probability functions of the various lines, to calculate the variation of the intensities of these lines as the pressure is reduced. Hence, by comparing the calculated intensity-variations with those found experimentally it is possible to test the validity of various distribution functions, and thus to find the formula which represents the distribution of the energies of the electrons in the discharge. The empirical formula which has been found in this way to account most satisfactorily for the experimental results may be expressed approximately in the following equation:

$$dN_1 = N_1 (2{\cdot}07\, f e^{-3y/2} + 0{\cdot}7\, (1-f)\, e^{-0{\cdot}4y^2})\, y^{\frac{1}{2}}\, dy \qquad \ldots\ldots(2),$$

where

$$f = 1{\cdot}882 . 10^{-3},$$

so that $(1-f)$ is practically unity.

This equation may be regarded as expressing the fact that the energies of a small fraction $2 . 10^{-3}$, of the total number of electrons are distributed according to Maxwell's formula, while the distribution of the energies of the vast majority of the electrons is represented by a formula very similar to the diffusion distribution of (1).

The mean energies of the two groups are the same, and it is the smaller group that is of predominating influence at the higher pressure as far as excitation and ionization in the positive column are concerned. It is suggested that this formula is valid over a very wide range of pressures, 0·32–40 mm. ($1 < Z/p < 4$) when f is practically constant. However it should be realized that in reality f is not actually constant, but is a function of the energies of the electrons and atoms. Thus when Z/p is practically zero or very small the mean loss of energy of the electron is zero, the distribution is Maxwellian, and $f = 1$. When Z/p increases f decreases, and the process of diffusion begins to affect the distribution. Finally when Z/p is very large f vanishes and the distribution is entirely controlled by diffusion, on the assumption that only elastic collisions occur.

In order to calculate the relative intensities of any line at various pressures it is first necessary to consider the probability of excitation of that line by electron impact, which is a function of the energy of the electron that excites it.

§ 4. THE EXCITATION FUNCTION

There have been many experimental investigations[11, 12, 13, 14] of the excitation of the helium atom by electron impact, and these experiments show that the probability of excitation increases from zero to a maximum value, when the energy of the electron is increased above the excitation energy V of the atom. The actual shape of the excitation function when plotted as a function of the energy E_x of the electron is different for the different lines, but there is a marked family likeness between the curves for those lines which belong to the ortho-helium system, and also between the curves for those which belong to the par-helium system.

For example, while the excitation curve for each state shows a maximum value corresponding to a certain energy E_m of the colliding electron, the sharpness of the E_m

maximum depends on the system to which the lines belong. In general, lines belonging to the singlet system have excitation curves with broad maxima at a high energy roughly corresponding to about 80 V., while the excitation curves of the triplet lines show sharp maxima at energies E_m of about 30 V. It is the differences in the form of the excitation functions of these lines which have approximately equal excitation energies that accounts for their different behaviour as the pressure of the gas in the discharge tube is changed. For the purposes of this investigation it is only necessary to find simple expressions which approximate to the actual forms of the probability-of-excitation curve determined experimentally. For instance, the excitation curves of those lines which rise sharply to a maximum value may be represented by the equation

$$P=k, \quad V<E_x<\infty \qquad \text{.....(3),}$$

where P is the excitation function and k is a constant.

For example, such lines are λ 5016 and λ 4713.

Moreover, for many triplet lines we may take

$$P=k\,(E_x-V)/E_x, \quad V<E_x>E_m$$
$$P=0 \qquad\qquad E_x>E_m \qquad \text{.....(3').}$$

This form is suitable for lines such as λ 5876, λ 3889. Now, owing to the form of the distribution curves expressed in equation (2), the number of electrons with energies greater than any given value V diminishes rapidly as V increases. When V is about 5 times the mean energy E_1 the integration of the formula (2) between the limits V and $3V/2$ is practically identical with integration between the limits V and infinity. Hence the exact shape of the probability curves for values of the energy of the electrons greater than $3V/2$ is not of much importance because in this case the important part of the curves is that in the immediate neighbourhood of the excitation energy. Unfortunately, the experimental determination of the form of the probability functions of the various lines in the immediate vicinity of their excitation energies is beset with great difficulty. The determinations are only approximate for this region, and there is no exact agreement in the values found by various observers.

However, it is interesting to note that when the mean energy of the electrons in the discharge is very low (<3 V.) the number of electrons with energies greater than, say, 25 V. may be neglected in comparison with the number with energies greater than, say, 23 V. Thus in this case the only important range of the excitation function of the various lines is that lying between the energies corresponding to 23 and 25 V. Now, as far as can be seen from the experimental determinations the excitation-probability curves for all the various lines have the same shape within this narrow range. Hence it follows that the behaviour of all the lines in the visible spectrum will be practically the same if their excitation energies are not very different. This accounts for the fact that the intensities of all the lines in the radiation from the helium glow discharge, which were measured by Keyston, increased in exactly the same ratio when the pressure of the gas was reduced from

40 to 7 mm. corresponding to a change of mean energy of the electron from 2·58 to 3·85 V.

However, at the lower pressures, when the mean energy of the electron is greater than 3·85 V., the number of the electrons with energies greater than say 25 V. can no longer be neglected in comparison with the number with energies greater than 23 V. Thus in this case it is necessary to take into consideration the different forms of the excitation function for the different lines.

§ 5. THE CALCULATION OF THE RELATIVE INTENSITIES OF THE LINES AT DIFFERENT PRESSURES

When an atom is in an excited state, in general, more than one transition to a lower level is possible. In the case of the helium lines under consideration, and given in table 1, the only exception is in the transition $2^3S - 3^3P$ (λ 3889), as this is the only one allowed from the 3^3P level. However, in each case the number of transitions from any given excited state is proportional to the number of atoms in that excited state, though only in the case λ 3889 is the number of transitions equal to the number of excited atoms.

However, in this paper only the relative intensities of each of the lines at various gas pressures are being considered, and the relative intensities of any given line are proportional to the relative numbers of the excited atoms at those pressures.

The intensity of the light of a certain wave-length which is emitted from the glowing gas is proportional to the number of atoms in a certain excited state, and it does not depend on the way in which that state has been excited. Now an atom may be put into a given excited state by any of the following processes: (i) a single collision with an electron, (ii) two successive collisions involving two electrons, (iii) the emission of radiation by the atom when in a higher excited state, (iv) the recombination of a helium positive ion and an electron. However, in those cases[1] in which the intensity of the radiation emitted from the helium positive column has been measured it has been found to be directly proportional to the current, and this result is in agreement with the experiments of Lees[14], in which the gas was excited by a homogeneous beam of electrons from a filament. Thus it follows that the atoms are not excited by any process requiring a double electron impact. Again, for large quantum numbers the classical rule governing transitions between various states is approximately valid. Thus the intensity of a line of frequency ν, measured by the number of quanta emitted per second by the atoms due to transitions between states which differ in energy by $h\nu$, is proportional to ν^3, so that the probability of successive changes in energy levels involving the emission of low-frequency radiation is low, and it may be neglected in comparison with the probability of transitions involving the emission of lines of the shortest possible wave-length. Further, it has been shown previously[2, 16] that no appreciable radiation is emitted from a positive column of a discharge as a result of the process of recombination. The most favourable conditions for recombination in a dis-

charge tube obtain in the Faraday dark space, and no appreciable light is emitted from this region. There is no recombination in the body of the glowing gas in the positive column as the ions and electrons recombine at the walls of the tube, towards which they are driven by the action of diffusion and the radial electric field set up by the charge in the gas.

Thus it may be assumed that the excitation of the radiation emitted from the positive column in the discharge is due principally to the single collisions of the atoms of the gas with electrons of high energy.

Consider the uniform positive column in a wide cylindrical discharge tube, and let the total number of electrons in 1 cm. length of tube be N_1. Then if the energies
dN_1 of the electrons are distributed according to equation (2) the number dN_1 of electrons with energies lying between E_x and E_x+dE_x is proportional to

$$(Be^{-3y/2}+e^{-0\cdot4y^2})\, y^{\frac{1}{2}}\, dy,$$

where B is a constant equal to $5\cdot38.10^{-3}$.

n, q_i If n is the number of atoms per cm^3 at a pressure of 1 mm. and q_i is the cross section of an atom for excitation to a given state, then the number of excitations to that state per sec. per cm. of column due to collisions with electrons of energy E_x
p_1 in the gas at pressure p_1 is proportional to

$$dN_1 p_1 n q_i\, (2eE_x/m)^{\frac{1}{2}} \qquad \ldots\ldots(4).$$

q_k Now if q_k is the gas-kinetic cross section of an atom, then $q_i=Pq_k$, where P is the probability of excitation by electron impact. It is now necessary to consider separately the two forms of the function P as given in equations (3) and (3′).

(i) Let $P=k$ when $E_x>V$.

I_1 Then the total number I_1 of excitations per second is obtained by integrating the expression (4) from V to infinity. Thus

$$I_1=\int_V^\infty Cp_1E_1^{\frac{1}{2}}\,(Be^{-3y/2}+e^{-0\cdot4y^2})\, y\, dy,$$

where C is a constant equal to $0\cdot8N_1knq_k\,(2e/m)^{\frac{1}{2}}$. Hence the intensity I_1 is proportional to

$$N_1p_1\,[B\,(V+2E_1/3)\,2E_1^{-\frac{1}{2}}/3\,e^{-3V/2E_1}+1\cdot25\,E_1^{\frac{1}{2}}\,e^{-0\cdot4\,(V/E_1)^2}] \qquad \ldots\ldots(5).$$

(ii) Now consider the alternative form of the function P given in equation (3′). The number of excitations per second is given by

$$I_1=\int_V^\infty Cp_1\,(1-V/E_1y)\,y^{\frac{1}{2}}\,(Be^{-3y/2}+e^{-0\cdot4y^2})\,dy,$$

so that in this case the intensity I_1 is proportional to

$$N_1p_1\left[4B/9\,E_1^{\frac{1}{2}}\,e^{-3V/2E_1}+1\cdot25E_1^{\frac{1}{2}}\,e^{-0\cdot4\,(V/E_1)^2}\right.$$
$$\left.-0\cdot79\sqrt{\pi}\,.\,V\,E_1^{-\frac{1}{2}}\,\frac{2}{\sqrt{\pi}}\int_\xi^\infty e^{-\xi^2}\,d\xi\right] \qquad \ldots\ldots(5'),$$

where $\xi=0\cdot648V/E_1$.

The value of the integral in expression (5′) can be obtained from tables[17]. Owing to the presence of this integral the function represented by (5′) does not increase with E_1 as rapidly as the expression (5). Thus the form of the excitation function given in equation (3) is adopted for calculating the intensities of those lines which increase very rapidly as the pressure is diminished, such as the lines λ 3188, λ 5016 and λ 4713, while the form of P given by equation (3′) may be adopted in the case of the lines λ 5876, λ 6678, λ 3889 and λ 4471. Let the two values of I_1 given at (5) and (5′) be represented by

$$p_1 N_1 \phi\,(E_1).$$

Then the ratio of the intensities of a line at the two different pressures p_1 and p_2 is given by

$$I_1/I_2 = p_1 N_1 \phi\,(E_1)/p_2 N_2 \phi\,(E_2).$$

When the current is the same at both pressures then $N_1 W_1 = N_2 W_2$, so that

$$I_1 = I_2 W_2 p_1 \phi\,(E_1)/W_1 p_{12} \phi\,(E_2) \qquad \text{.....(6).}$$

The values of the function ϕ can be calculated for any value of E_1, that is, of p_1. Thus if the intensity I_2 of any given line at a pressure p_2 equal to 7 mm. is taken to be 100, then the intensity I_1 at any other pressure p_1 can be found from equation (6).

These calculated values for the relative intensities of the lines are given in table 1, in which the form of excitation function and the value of the excitation potential V for each line also are given.

Table 1. The intensities of the helium lines calculated from equation (6)

Pressure of gas in discharge	λ 5876 $2^3P - 3^3D$ $V = 22{\cdot}96$ $P = k(E_z - V)/E_z$		λ 4471 $2^3P - 4^3D$ $V = 23{\cdot}62$ $P = k(E_z - V)/E_z$		λ 3889 $2^3S - 3^3P$ $V = 22{\cdot}89$ $P = k(E_z - V)/E_z$		λ 3188 $2^3S - 4^3P$ $V = 23{\cdot}59$ $P = k$		λ 4713 $2^3P - 4^3S$ $V = 23{\cdot}4$ $P = k$		λ 5016 $2^1S - 3^1P$ $V = 22{\cdot}97$ $P = k$		λ 6678 $2^1P - 3^1D$ $V = 22{\cdot}96$ $p = k(E_z - V)/E_z$		Z/p†
	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	
40	12	5	10	7	9	5	<9	9	—	7	13	8	12	5	1·29
30	19	11	18	12	17	11	—	17·5	—	12	21	19	19	11	1·38
20	34	16	27	23	27	16	—	31	—	23	35	29	33	16	1·51
13	58	26	50	60	50	26	46	70	48	60	58	57	57	26	1·73
7	100	100	100	100	100	100	100	100	100	100	100	100	100	100	1·94
4	148	120	220	130	163	120	220	150	220	130	155	120	145	120	2·10
1·5	252	157	540	300	334	156	616	360	594	360	418	310	261	157	2·50
0·78	340	450	675	600	367	400	920	920	772	900	668	750	340	450	2·9
0·32	187	540	585	560	550	500	1200	1165	868	1100	1600	1100	303	540	3·85

* Experimental data after Keyston[3]. † Z is the r.m.s. value of the force in the h.f. discharge.

Some typical results are also represented in the curves of figures 1 to 4. The ordinates represent the intensities of the various lines when their intensities at a

pressure of 7 mm. are taken to be 100, and the abscissae represent the mean energy of agitation of the electrons. The corresponding pressures also are marked. The different behaviour of the various lines is well illustrated by the curves; thus the intensities of some of the lines continue to increase as the pressure is diminished, while other lines become fainter at the lowest pressures.

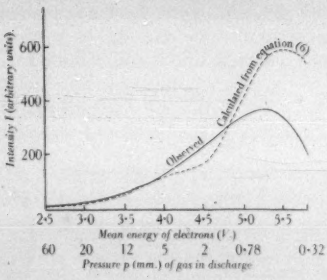

Figure 1. λ 5876 2^3P-3^3D; λ 6678 2^1P-3^1D.

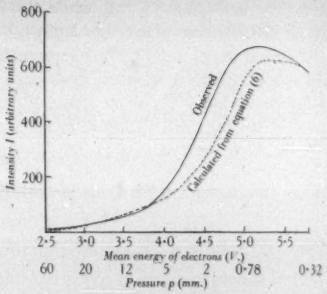

Figure 3. λ 4471 2^3P-4^3D.

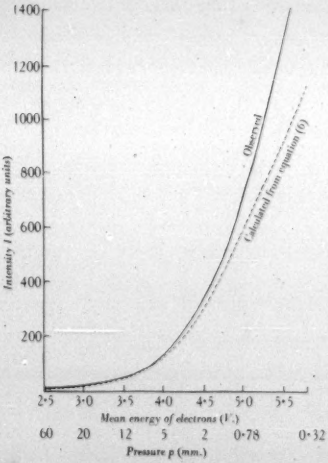

Figure 2. λ 5016 2^1S-3^1P.

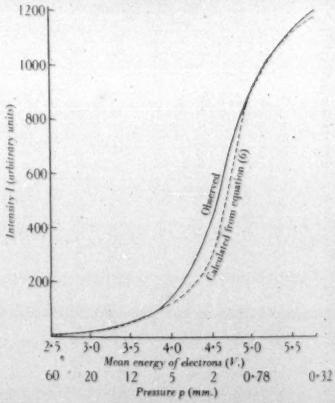

Figure 4. λ 3188 2^3S-4^3P.

§ 6. CONCLUSION

The curves show that there is a general agreement between the calculated and the observed variation of the intensity of the spectral lines as the pressure of the gas is altered. This result then supports the conclusions regarding the nature of the

distribution of the energies of the electrons which were arrived at in § 3. However, the agreement is not perfect and there are many causes which might give rise to the discrepancies between the theoretical and experimental curves. Firstly, as was pointed out above, the exact nature of the excitation functions of helium in the immediate neighbourhood of the excitation potentials of the various states is unknown; but there are theoretical and experimental considerations which indicate that the simple formulae of equations (3) and (3′) are reasonable expressions of these functions, at least as far as their application in this case is concerned. Again, the variation of the mean free path of the electrons with their velocity—the Townsend-Ramsauer effect—was neglected in the derivation of the distribution formula. The mean free path L, at 1 mm. pressure, of electrons with various energies has been measured by Townsend's method[4] at low velocities and by Ramsauer's method[18] at high velocities, and the variation may be seen from the following table 2:

Table 2

E_x (V.)	1·85	3·7	5·2	10·7	15·8	19·2
L (cm. $\times 10^{-2}$)	4·8	5·2	5·5	6·7	8·3	9

This variation of the mean free path will not alter the form of the expression for the distribution but only the numerical coefficients in it. That is, the width of the distribution will be affected by the changes in L. In the case in which the free path diminishes as the energy of the electron is increased, the distribution would tend to become narrow. This effect occurs in argon, where the mean free path diminishes when the energy of the electron increases up to 10 V., and MacCallum, Klatzov and Keyston[19], from a study of the continuous spectrum of that gas, have been led to the conclusion that the distribution in it is very narrow. Alternatively, table 2 shows that in helium L increases with E_x, so that the proportion of faster electrons is increased. This may account for the fact that a numerical coefficient 0·4 in the exponent in the distribution formula (2) gives better agreement in the above curves of relative intensities than does the theoretical value 0·55, which is obtained on the assumption that the mean free path is independent of the velocity. Further, a modification of the form of the distribution formula is required owing to the variations of the fractional loss of energy at a collision about the mean loss. Townsend has pointed out previously that the actual distribution is wider than that expressed by the simple diffusion expression (1) as due to this effect alone. However, the widening of the distribution from these causes is to some extent offset by the reduction in the number of fast electrons due to collisions resulting in excitation and ionization in which large losses of energy occur. On the other hand the maximum efficiency of ionization in helium by 100 V. electrons is only about 10 per cent and it is much less for excitation.

The original experiments on the motions of electron gases were interpreted[15] on the basis of the older kinetic theory in which the collision between electrons and atoms of the gas were considered to resemble those between uncharged elastic spheres. Consequently the scattering of the electrons in collision with the atoms of

helium was considered to be uniform. However, the scattering of electrons by helium is not perfectly uniform; but the angular distribution of the scattered electrons is not very different from that which obtains in the case of uniform scattering, so that no great error is introduced from this cause. Non-uniform scattering would have to be taken into consideration if the mean energies E_1 were calculated from the measured ratio Z/p; it should be emphasized, however, that the values of E_1 used in the calculations were not deduced from the values of Z/p but were the observed values found in the experiments of Townsend and Bailey for the corresponding values of Z/p.

Further, it should be realized that the only theoretical distribution formula possible under the conditions laid down in § 3 is that expressed[6] in equation (1). On the other hand, equation (2) merely gives an expression with which it is possible to calculate the variation of the intensities of the spectral lines and of the force[10] in the positive column of high-frequency and direct-current discharges in helium, and to find general agreement between the calculated rates of variation and those determined experimentally. This result supports the contention that when $Z/p < 4$ the actual distribution formula for the energies of the electrons in helium, and most likely in the other monatomic gases, is that given in equation (1) but that it is essential to take into consideration the variation of the mean free path of the electrons with velocity.

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DISCUSSION

Dr R. Winstanley Lunt and Mr C. A. Meek. (1) The distribution formula. The author does not give the formal derivation of the distribution formula which he now advances. Emeléus, Cowan and Brown* were able to account for the relative intensities of the lines $\lambda\lambda$ 5016, 4713 in the positive column and in the negative glow on the assumption of a Maxwellian electron-energy distribution in each of these zones. There are experiments on positive-column discharges in many gases for which Langmuir probe data indicate that the distribution is sensibly Maxwellian. (2) The excitation functions. Whilst the exact shape of the excitation functions in the neighbourhood of the critical potential is difficult to determine experimentally, the theoretical calculations of the excitation functions in helium are for the most part in agreement with the experimental determinations of Lees†; furthermore, it would be hard to find in these calculations‡ any justification for the particular approximate expressions selected by the author. The author points out that the excitation functions for lines belonging to the singlet system are characterized by broad maxima, whilst those of the triplet systems show sharp maxima. For "those lines which rise sharply" he suggests that the excitation function can be represented by his equation (3) and cites as an example λ 5016; this however is a singlet line $3\,^1\mathrm{P} - 2\,^2\mathrm{S}$, and its excitation function rises slowly to a broad maximum at about 100 volts.‡ Further, the author points out there is a "marked family likeness" between the curves belonging to a single system, but he has selected different approximate expressions for the excitation functions of two levels belonging to the same system, $3\,^3\mathrm{P}$ $[\mathrm{P} = k\,(E_x - V)/(E_x)]$, and $4\,^3\mathrm{P}$ $(\mathrm{P} = k)$. (3) Conclusion. Whatever may be the truth about the validity of the distribution function proposed by the author, his arbitrary selection of different approximate expressions for the excitation of lines of the same system, and of expressions which do not approximate sufficiently to the experimental data, tends to destroy, we believe, in a great measure the evidence now adduced by him in support of this distribution.

Author's reply. (1) The distribution formula. With regard to the paper by Emeléus and others, the authors themselves state "we find that the distribution of velocity of electrons is not Maxwellian in the negative glow", and they make no mention of any conclusions regarding the distribution of energies in the uniform positive column over any range of pressures. Again, if we refer to a later paper§ by the same authors, also on probe measurements of the distributions in a helium discharge, we find no evidence presented there which indicates that the distribution in the uniform positive column is Maxwellian, and the authors do not suggest such a conclusion.

(2) Excitation functions. It was pointed out in § 4 that the steepness of the excitation curve is only important near the critical potential, owing to the low mean

* Emeléus, Cowan and Brown, *Nature*, Lond., **127**, 593 (1931); Cowan, Thesis, Belfast, 1931.
† Massey and Mohr, *Proc. roy. Soc.* A, **132**, 605 (1931); **140**, 613 (1933).
‡ Lees, *Proc. roy. Soc.* A, **137**, 173 (1932).
§ Emeléus, Brown and Cowan, *Phil. Mag.* **17**, 146 (1934).

energies of the electrons in the positive column and the narrowness of any reasonable distribution, so that a broad maximum in the curve at about 80 V. is of negligible consequence. Also in the relevant range of energy V to $3V/2$ the general distinction between the two systems of lines is not very pronounced, the marked family likeness for lines of the same system being more noticeable for energies greater than about 30 V. The excitation curve for the line λ 5016 (see Lees[14]) may be well represented by the equation $P=k(E_x-V)$ when $E_x<80$ V. However, when this expression is used, the relative numerical values of the integral differ little from those of the integral (5), but as the expression itself is more complicated the simpler one of equation (5) is used as a sufficient approximation. The following are the reasons which lead to the adoption of the same formula, $P=k(E_x-V)/E_x$, to represent the initial stages of the excitation curves for the lines λ 5876, 3889, 6678, it being remembered that $P=0$ when $E_x>V_m$ for the two triplets, λ 5876 and 3889, and that k depends on their respective atomic cross-sections. Now the change in intensity of any line emitted from the helium positive column when the pressure of the gas is altered depends on its excitation potential, on the shape of its excitation curve in the initial range 23 to about 30 V., and on the mean energies and distribution function of the electrons. When the behaviours of two lines emitted from the same tube are being compared the last two factors are the same for both lines, so that any difference in their behaviour must be accounted for by differences in excitation potentials and curves. But the lines $\lambda\lambda$ 5876, 6678 have practically the same excitation potentials and almost identical behaviour throughout the whole range 40 mm. to 0·8 mm. Hence it follows that the excitation curves of these lines have the same form within the relevant range of energies although one line is a triplet and the other a singlet. Also, the critical potential and the general variation of intensity is nearly the same for λ 3889 as for these two lines, so that the same function P was adopted. Hence it it is considered that, within this range, the approximations given and discussed in § 4 of the paper are reasonable, and are not so much in error as to throw grave doubt on the validity of the results derived from them.

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DEMONSTRATION

An experiment illustrating the support of a weight by a vertical tube containing sand, the lower end being covered by a thin membrane*

Demonstration given by Major C. E. S. Phillips, O.B.E., February 7, 1936

This demonstration formed part of a series of experiments shown by me at the Royal Institution in 1910 to illustrate a discourse there upon "Electrical and other properties of sand".

Dry sand emitted from a nozzle and falling upon a horizontal surface forms a cone, the angle at the base of which is 35°. It follows that sand flowing into a metal tube closed at the lower end first forms such a cone the base of which is limited by the diameter of the tube, so that if further sand enters the tube its particles roll down the slope of the cone first formed. As the tube fills up it may therefore be regarded as containing the original cone at the lower end and successive layers of particles which arrange themselves so as to preserve the original angle of slope, viz. 35° with the horizontal.

If such a column be gently tapped so as to pile or lock the grains and a vertical downward force be applied to the sand column, it is seen that this force is so resolved that only a small fraction of it reaches the cone at the base of the tube. If the walls of the tube are rigid, considerable weights can be thus supported by the column, owing to increased friction between the sand and the inner surface of the tube, it being only necessary to close the lower end with a thin membrane which is capable of supporting little more than the weight of the small cone of sand in contact with it.

In order to show this I have arranged a flanged vertical brass tube open at both ends, which projects through an arm of a kind of gallows. The diameter of the tube is 0·5 in. and the lower end is closed by a piece of cigarette paper held in position by means of a rubber ring. Enough white sand is now poured into the tube to stand about 3 in. above the thin paper. The tube is then gently tapped with a light hammer and a loose plunger is inserted from the top end carrying a cross piece with a ring at each end. An attempt to suspend Dr Ferguson from the rings will be made. It will appear as though his weight (21 st.) is supported by the thin cigarette paper.

The experiment was successfully carried out.

* See also a paper by J. H. Shaxby and J. C. Evans on "The variation of pressure with depth in columns of powders", *Trans. Faraday Soc.* **19**, Part 1 (May, 1923).

REVIEWS OF BOOKS

Faraday's Diary: being the Various Philosophical Notes of Experimental Investigation made by Michael Faraday, D.C.L., F.R.S., during the years 1820–62.* Vol. **5** (Sept. 6, 1847–Oct. 17, 1851), pp. xiii + 456; vol. **6** (Nov. 11, 1851–Nov. 5, 1855), pp. xiv + 495; vol. **7** (Nov. 24, 1855–March 12, 1862), pp. xvii + 465; Index, pp. 64. (London: G. Bell and Sons.) Seven volumes and index. £12. 12*s.* the set.

In these last three volumes of the *Diary* we find, among other things, the details of Faraday's experiments on the magnetism of flame and other gases, and of his work on the behaviour of crystals in the magnetic field—the investigation of "magnecrystallic action" which is the subject of a well-known tribute from Tyndall to his predecessor. There is also the extensive development of the method of representing magnetic fields by lines of force, illustrated by fine reproductions of some of Faraday's filings maps. The last volume contains a full account of observations on the properties of precipitated gold; these are no doubt well known to physical and colloid chemists, but many physicists will be surprised to discover the extent and variety of Faraday's experiments with gold sols.

Of greater general interest, however, are the entries that relate to Faraday's protracted search for a connexion between gravity and electricity, and others which show his continued preoccupation with the relation between light and electromagnetism. In fact there can be no doubt that Faraday, though in the years under review he may be said to have passed the zenith of his career as an *experimental* philosopher, was nevertheless doing much to shape a general electromagnetic theory of light. Here is a typically significant passage (§ 14233, January 19, 1856): "Still, it is not absolutely certain that magnetic propagation, if in an (or the) ether, must be as quick as light, though it is likely."

Of more special interest to physicists of a later generation are Faraday's experiments on the light from a source situated in a strong magnetic field. It has been generally known for some time, from the writings of Bence Jones, Maxwell and Silvanus Thompson, that these were the last experiments that he undertook; they are described in the closing passages of the *Diary*, and Faraday was in his 71st year when he entered them. It is perhaps less well known that he had attempted similar experiments almost nine years earlier. Thus (May 16, 1853, §§ 13053 *et seq.*): "In regard to the possibility of the Magnetic force affecting (*sic*) a change in the character of rays *emanating* from an object place[d] in the center of an intense magnetic field... the flame examined whilst submitted to the intermit[t]ed action of the magnet. Its light examined by the prism shewed no sensible difference whether the magnetism was on or off. It shewed no difference when examined in various ways by polarizers, i.e. Nicol's prisms."

It is worth while stressing here the two respects in which this work is absolutely typical of Faraday's methods of research. In the first place, in all his experiments on light it was almost a matter of routine to test for polarization effects. Secondly, to quote Tyndall (*Faraday as a Discoverer*, p. 89), "One great source of his success was the employment of extraordinary power... he never accepted a negative answer to an experiment until he had brought to bear upon it all the force at his command." Thus we see from the closing passages of the *Diary* how, having acquired a new Steinheil spectroscope, he applied it at once in the repetition of an experiment abandoned nine years earlier.

It is evident therefore that only the inadequacy of the technical resources of his time prevented Faraday from anticipating at least a part of Zeeman's magneto-optical dis-

* Vols. 1–4 were reviewed in these *Proceedings*, **45**, 358 (1933) and **46**, 484 (1934).

coveries. Zeeman, who inscribed his *Researches in Magneto-Optics* "to the Memory of Michael Faraday", was at first unaware of Faraday's unsuccessful attack upon the same problem. He has however recorded that at a later stage he was encouraged to persevere in his own attack by discovering that Faraday had considered the experiment worthy of trial.

In an *Encyclopaedia Britannica* article (reprinted in vol. **2** of his collected papers) Maxwell referred to Faraday's "concentration of his efforts in seeking to identify the apparently different forces of nature, his far-sightedness in selecting subjects for investigation, his persistence in the pursuit of what he set before him, his energy in working out the results of his discoveries, and the accuracy and completeness with which he made his final statement of the laws of the phenomena".

For evidence of these qualities we need look no further than the pages of the *Experimental Researches*, but many of them are seen in greater perfection in the *Diary*. We have therefore every reason to be grateful to the Managers of the Royal Institution for the great service they have done in giving the *Diary* to the public, and for giving it in so handsome and dignified a form. Credit must here be given also to the publishers and the Cambridge University Press for their shares in the production.

Mr Martin is to be warmly congratulated upon the wholly admirable way in which he has edited Faraday's manuscript. It must have been an onerous as well as a difficult task, and it is not altogether surprising that a faintly plaintive note is to be detected at the end of his preface to vol. **7**. He may however derive some satisfaction from the thought that the task was well worth doing, and the assurance that it could not have been better done.

H. R. R.

Atomic Physics. By MAX BORN. Translated from the German Edition by J. DOUGALL. Pp. xii + 352. (London: Blackie and Son.) Price 17*s*. 6*d*.

This is a really excellent introduction to practically the whole range of atomic physics, and it deserves the highest praise. The book deals mainly with problems of atomic structure and with recent developments of quantum theory. In addition there is an excellent summary of experimental work in nuclear physics.

The treatment is suited to the needs and capacity of the average honours student. Most of the necessary mathematics is concentrated into a number of appendices which together occupy about one quarter of the whole volume. The main text may therefore be regarded as popular in the best sense of this frequently abused word—that is, it may well appeal to many non-specialist readers who want simple but trustworthy expositions of such topics as quantum statistics and nuclear spin.

As would be expected from an eminent theoretical physicist, Dr Born (to quote from his own preface) has "naturally placed the theoretical interpretation of phenomena well in the foreground". His outlook is however that of a mathematician who has always maintained a close connexion with the laboratory, and his treatment will not be found too austere for the average experimentalist.

The only adverse criticism which can fairly be made is on a matter of detail—the accuracy of the dates which have been inserted "to serve as a historical guide". The intention is excellent; in a book of this size there is obviously no space to spare for historical details, and bare dates can at least serve as reference points for a later survey of the subject. It is however important that the reference points should be correct—more especially just now, when there is in some quarters an evident disposition to rewrite the history of science, and even to re-shape it in terms of ethnographic or political theories. Some of Dr Born's dates are sufficiently inaccurate to mislead quite seriously the young student of the history of physics. For instance (p. 45), in discussing "electromagnetic mass" it is mentioned that

"the effect is the same as if the mass were increased by a part proportional to e^2/a (J. J. Thomson, Heaviside, Searle, about 1900)". In fact, Thomson gave this result (in the *Philosophical Magazine*) as early as 1881, and the period quoted ("about 1900") belongs to a quite different epoch in the history of electrical theory. Again, it would be difficult to justify the attribution (p. 31) of the law of radioactive transformation to von Schweidler in 1905.

We do not wish to stress these points unduly, but the book is of such outstanding excellence that students may well be inclined to regard it as completely authoritative. There is therefore all the more reason for wishing to see it purged of inaccuracies.

Dr Dougall's translation—no doubt aided by a very lucid original text—is very good indeed, and the book is a notable addition to the physics student's select library of essential texts. Modern atomic physics is emphatically not a fit subject for the hack writer, and we are fortunate in getting this text from the pen of a leading original investigator. H. R. R.

Molekülspektren und ihre Anwendung auf Chemische Probleme, II Text, by H. SPONER. Pp. xii + 506. (Berlin: Julius Springer, 1935.) RM. 36, bound RM. 37.80.

The excellence of this volume of Dr Sponer's work comes as no surprise to a reader of the preceding volume (Tables), which was reviewed in November 1935 in these *Proceedings*. The completed work is cordially recommended to both spectroscopists and physical chemists. In the first two chapters are brief introductions to (I) the older quantum theory of atomic spectra and (II) the quantum mechanics. The third and longest chapter (205 pages) is devoted to diatomic and polyatomic molecular spectra. However, for reasons which will be evident from the full title of the work, certain aspects of these spectra are either omitted entirely or treated rather briefly. For example, infra-red spectra of diatomic molecules have been adequately covered (apart, of course, from the ever-growing numerical data) by Schaefer and Matossi's book in the same series. Again, the rotational line structure of the various types of electronic bands, the distribution of line-intensities in such bands, and the Zeeman effect have all been treated at some length in several well known books and reviews in recent years, and moreover are of comparatively little significance for the chemical problems to which Dr Sponer gives due prominence in the remaining four chapters (221 pages), namely, the derivation of chemically important quantities from band spectra (chapter IV), chemical binding and valency (chapter V), excitation of molecules by collisions with electrons, atoms, molecules and ions (chapter VI), and other chemical applications of the results of spectroscopic research (chapter VII). There are 87 figures, including a few spectrograms; figures 15–19 and 43 (pp. 51, 54 and 118) would be much improved by the provision of scales of wave-length or wave-number. The usefulness of the tables in vol. I is enhanced by the inclusion in this volume of a 29-page addendum of numerical data and references to papers which appeared up to autumn 1935. Tables and text are thus brought equally up to date. W. J.

A Class-Book of Magnetism and Electricity. By H. E. HADLEY. Pp. x + 512. (London: Macmillan and Co., Ltd., 1936.) 6*s*. 6*d*. net.

This comprehensive text-book is intended mainly to provide a course for School Certificate and Matriculation examinations, but is not confined to their syllabuses. In an introductory chapter on the principal effects of the electric current rather too much is attempted. Most beginners would find difficulty in grasping the analogy between gravitational and electric-current phenomena. The introduction is followed by a full treatment of magnetism, static electricity and current electricity. In the section on magnetism the

fields due to magnets and electric currents are rightly taken consecutively. Then we are given accounts of conduction through gases (including the photo-electric cell and thermionic valve), electric communications, wireless, and television. Practical applications are adequately treated, and the book is up to date. Suggestions for practical work are incorporated with the theory. Many chapters close with interesting historical notes, and there are numerous examination questions and worked examples. The book is well provided with diagrams and is attractively written. It will be welcomed by those who wish for a detailed elementary account of the subject.

A. D. H.

Magnetism. By E. C. Stoner. Pp. vi + 136 with 20 diagrams. (Second Edition, Revised 1936. Methuen's Monographs on Physical Subjects.) Price 3*s*. net.

The appearance of the second edition of this useful little book will be generally welcomed, for it would indeed be difficult to condense more knowledge of the modern aspects of magnetism in a smaller space without serious loss in clarity and important detail. The revision has been carefully done, and on the whole the book reads more easily than the first edition did. It is thoroughly recommended.

L. F. B.

Phenomena in High-Frequency Systems. By A. Hund. (McGraw-Hill Publishing Co., Ltd.) Pp. 642. Price 36*s*. net.

This book gives a comprehensive account of those portions of physics which have been applied to problems of radio-communication and to a smaller extent of line telephony. One gets the impression that the author has made a thorough search of the literature of the subject, made copious notes, and then arranged them under a dozen or so headings. The result is a book that will probably be consulted occasionally by many workers in search of information on particular points, but few will want to read the whole of it. The scope of the work may be judged by the following typical chapter headings: Space-charge devices, Phase-changers, Frequency-changers, Rectification, Piezo-electricity, The ionized layer, Directive systems, Recurrent networks. The treatment is, generally speaking, encyclopaedic in character, with a huge number of references to original papers. A somewhat jerky style and a singularly uncritical attitude towards the many investigations described make the reading of the book rather heavy work, but the author may fairly claim to have succeeded in his aim "to give a thorough up-to-date discussion of phenomena occurring in high-frequency systems, with many applications to problems arising in communication engineering".

L. H.

The New Acoustics. By N. W. McLachlan. Pp. vii + 166. (Humphrey Milford: The Oxford University Press, 1936.) 7*s*. 6*d*. net.

The scope of this volume may be gathered from its subtitle, "A Survey of modern developments in acoustical engineering", rather than from its title which might well include the word "applied". The need for some small book to form the counterpart of, say, Foch's more classical *Acoustique* in the Collection Armand Colin has been apparent for some time past to teachers if not to publishers; and it is therefore not surprising that Dr McLachlan, who within the last few months has published two monographs on acoustical topics, should now produce a third dealing with such subjects as anti-submarine devices, microphones, loud-speakers, gramophones, sound films, hearing and deaf aids, and architectural acoustics. As is to be expected the book has a definite engineering bias

and is clearly written and well illustrated, but the reviewer for one would willingly exchange a fifteen-page summary of pre-war acoustics for a few pages additional to, say, the eleven devoted to reverberation and absorption coefficients.

E. J. I.

Das akustische Beugungsgitter und seine Anwendung zur Schallspektroskopie. By ERICH THIENHAUS. Pp. vii + 59 with 21 illustrations. (Leipzig: J. A. Barth.) Price: RM. 2.40.

Prof. Erwin Meyer gave an account of this sound-grating spectrometer in a lecture at Bad Pyrmont two years ago and it has also been described in some detail in the Society's *Progress Reports*, **2**, 170 (1936). Suffice it to say here that the grating is made out of a row of equispaced nails round the arc of a circle on the principle of the Rowland grating. The reader who requires details as to its construction will find them given in this brochure together with a complete theory, and typical sound spectra analysed by the apparatus.

E. G. R.

A Fugue in Cycles and Bels. By JOHN MILLS. Pp. 269. (Chapman and Hall.) 13*s.* 6*d.*

It is a popular fallacy, fostered by certain universities which provide easy matriculations for would-be graduates in music, that the musician is less endowed with intelligence of worldly matters than the average of his fellow-men. To a certain extent this notion would seem to be fostered by musicians themselves. One suspects that the faint praise with which the fraternity damn Mendelssohn is to a certain extent due to envy for the ease with which this composer mixed dividends and divine inspiration. The author of the book under review tries hard to write down to what he evidently expects to be his readers' low standard of intelligence. "The book is written for those who may wish to know what science is doing to music and what it can do for music", and the author's method of doing this alternates between rather puerile wise-cracking and rather heavy technicalities. He is a telephone engineer and he has some most interesting things to tell us about the development of the telephone and the sense of hearing, but, one feels, less of importance to say about the scientific aspects of music. Thus one would have hoped for a chapter on the acoustics of musical instruments, and the chapter headed "Electrical Music" should have given him the opportunity to describe in detail the various forms of electrical musical instruments now available, a subject which is of great interest to the *modern* musician. As it stands, we rather fear that the book will not reach the public for whom it is meant. Is the author himself a musician? At times he appears to display a facetious contempt for the art. Such a statement as "Music hath power but surprisingly little except when it is played on the big bass drum" is scarcely likely to commend his work to the serious musician.

E. G. R.

Mathematical Tables. Vol. **5**. Factor table giving the complete decomposition of all numbers less than 100,000. Prepared independently by J. PETERS, A. LODGE and E. J. TERNOUTH and E. GIFFORD. Pp. xv + 291. (London, Office of the British Association, 1935.) Price 20*s.* net.

This, the third of the six volumes of *B.A. Tables* to be devoted to a question of the theory of numbers, gives the factors of all numbers from 1 to 100,000. In particular, therefore, it constitutes also a list of primes up to that point. The preface is perhaps even more valuable than the table itself. It gives what is probably the most complete list of

errata yet prepared with reference to earlier tables of comparable scope, and a bibliography of factor tables covering higher ranges, together with references to the main errata lists for them. As regards the present table itself, the arrangement is convenient and the typography excellent; the only means of judging the accuracy must be from the statements given in the preface as to the precautions taken to avoid errors. These seem to have been extraordinarily thorough and one may hope that the table is free from error, though natural scepticism may protest that this is surely impossible. The checking of such a table is peculiarly difficult, because unlike that of tables of analytic functions it can obtain no help from examination of differences. The fact that the table, after printing, was examined against three independent manuscripts is the chief, and surely a very efficient, safeguard.

J. H. A.

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 48, PART 4 *July* 1, 1936 No. 267

535·338.3:546.34

INTENSITIES IN THE PRINCIPAL SERIES OF LITHIUM

BY S. WEINTROUB, M.A., University College, Southampton

Received November 12, 1935. *Read in title March* 20, 1936

ERRATUM

Proc. Phys. Soc. **48**, 215 (1936)

For the title of the last review read
Electric Melting Practice, by A. G. ROBIETTE, B.Sc.

to the transition from the state r to the state s is given in ergs per second by r, s

$$I = N_r A_{rs} h\nu_{rs},$$

where N_r is the number of atoms in the state r and A_{rs} is the Einstein[1] spontaneous- N_r, A_{rs}
emission probability.

It is convenient to introduce a set of quantities called *oscillator-strengths* or *f numbers*† in terms of which the intensity is given by f

$$I = N_r (g_s/g_r).(8\pi^3 e^2 h/mc^3).\nu_{rs}^3.f_{rs},$$

i.e. the intensity is proportional to the cube of the frequency ν_{rs}, and to the f ν_{rs}
number.

The first wave-mechanical calculations of the transition probabilities were made by Schrödinger, Sugiura, and Kupper[2]. Dirac[3] has shown that the coefficients A_{rs} may be expressed in terms of the matrix amplitudes for the transition r to s. These will be considered in more detail in § 6.

Before the oscillator-strength of a line in the series spectrum of an atom can be estimated it is necessary to obtain the wave functions and the energies of the

† For a fuller discussion of the oscillator-strengths, see Condon and Shortley's *Theory of Atomic Spectra*, Chapter IV (Camb. Univ. Press, 1936).

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ABSTRACT. The effect of using orthogonal instead of non-orthogonal wave functions in the calculation of the oscillator-strengths (f numbers) of the first three lines of the principal series of lithium has been investigated. The Hartree self-consistent field method is employed to calculate the ($1s$) radial wave function, and the ($2s$) radial wave function is made orthogonal to the ($1s$) by linear combination. The orthogonal functions have been used to calculate the energies of the optical terms ($2s$), ($2p$), ($3p$) and ($4p$), and the f numbers of the first three lines of the principal series. Very satisfactory agreement with observed values is obtained for the energies (the maximum difference being 3 per cent). The agreement for the f numbers is not so good, but is better than when non-orthogonal functions are used.

§ 1. INTRODUCTION

QUANTUM theory considers emission of radiation by atoms or molecules to take place as the result of a transition from a state of higher to a state of lower energy. The emitted intensity I of the spectral line corresponding to the transition from the state r to the state s is given in ergs per second by

I

r, s

$$I = N_r A_{rs} h\nu_{rs},$$

where N_r is the number of atoms in the state r and A_{rs} is the Einstein[1] spontaneous-emission probability.

N_r, A_{rs}

It is convenient to introduce a set of quantities called *oscillator-strengths* or *f numbers*† in terms of which the intensity is given by

f

$$I = N_r (g_s/g_r) . (8\pi^2 e^2 h/mc^3) . \nu_{rs}^3 . f_{rs},$$

i.e. the intensity is proportional to the cube of the frequency ν_{rs}, and to the f number.

ν_{rs}

The first wave-mechanical calculations of the transition probabilities were made by Schrödinger, Sugiura, and Kupper[2]. Dirac[3] has shown that the coefficients A_{rs} may be expressed in terms of the matrix amplitudes for the transition r to s. These will be considered in more detail in § 6.

Before the oscillator-strength of a line in the series spectrum of an atom can be estimated it is necessary to obtain the wave functions and the energies of the

† For a fuller discussion of the oscillator-strengths, see Condon and Shortley's *Theory of Atomic Spectra*, Chapter IV (Camb. Univ. Press, 1936).

normal and excited states of the atom. For hydrogen this presents no difficulty as, on account of the inverse-square-law character of the field, the wave equations can be solved exactly. However, for the many-electron atoms an exact solution of the problem of the determination of the wave function is not known, but approximations to it have been made by Hartree[4], Slater[5], and Fock[6].

Hargreaves[7] used Hartree's method for the numerical solution of the Schrödinger wave equation for an atom with a non-Coulomb field of force, to estimate the oscillator strengths of the lines in the principal series of lithium. Hartree's method does not take into account either the effects of interchange of electrons between the one-electron wave functions, or Pauli's principle. Slater[5] has shown how, by using a more accurate form of the wave function, it is possible to take into account the effects of interchange, and to calculate the energies of the optical terms from the parameters of the central-field problem and corresponding one-electron wave functions. McDougall[8], basing his work on Slater's, has calculated the optical terms of Si^{+3}; the stationary states there calculated are essentially states of a series electron outside a core consisting of closed shells; the perturbation of the core by the series electron is then small and can be neglected, so that the states of Si^{+3} can be taken as a Si^{+4} structure with an additional wave function for the series electron.

We shall adopt here a similar simplification, namely that the states of lithium may be taken as a Li^{+} structure with an additional wave function for the series electron. Slater's results, in so far as they are required for this paper, are briefly restated in §§ 2 and 3.

The object of this paper is to compare the oscillator strengths f, using different approximations to the one-electron wave functions. The ($2s$) wave function used by Hargreaves was not orthogonal to the other one-electron wave functions. The author has calculated the ($1s$) wave function, and the ($2s$) wave function is made orthogonal to the ($1s$). Next, the energies of the normal and excited states are calculated by Slater's and McDougall's methods, by means of these orthogonal wave functions. Finally, the oscillator-strengths for the ($2s$–$2p$), ($2s$–$3p$), and ($2s$–$4p$) transitions calculated from (a) non-orthogonal wave functions of Hargreaves, (b) orthogonal wave functions of the author, and (c) Fock wave functions, are compared with one another.

§ 2. GENERAL THEORY

Ψ The wave function Ψ of the stationary states of an atomic system consisting of
n n electrons are given by making $\int \Psi H \Psi^* d\tau$ stationary for a normalized Ψ,† where
H H is the Hamiltonian operator defined by the equation

$$H = \sum_{j=1}^{n} [-\tfrac{1}{2}\nabla_j^2 - N/r_j] + \sum_{j=1}^{n} \sum_{k=j+1}^{n} 1/r_{jk} \qquad \ldots\ldots(1),$$

N for an atom of atomic number N.‡ We have neglected the spin and relativity contributions to the Hamiltonian.

† Cf. Condon and Shortley, *Theory of Atomic Spectra*, Chapter VI.
‡ Atomic units are used throughout. For these, see Hartree[4].

Let us denote the individual electron wave functions by $\psi(\alpha/1), \psi(\beta/2), \ldots, \psi(\omega/n)$ where the Greek letters $\alpha, \beta, \gamma, \ldots, \omega$ refer to the wave functions and the numbers $1, 2, 3, \ldots, n$ to the coordinates (including spin) of the electrons. ψ; $\alpha \ldots \omega$; $1 \ldots n$

A general form of Ψ which conforms with Pauli's principle is the antisymmetric form, written as a determinant, thus

$$\Psi = \frac{1}{\sqrt{(n!)}} \begin{vmatrix} \psi(\alpha/1) & \psi(\beta/1) \ldots \psi(\omega/1) \\ \psi(\alpha/2) & \\ \vdots & \\ \psi(\alpha/n) & \psi(\omega/n) \end{vmatrix} \qquad \ldots\ldots(2).$$

It is usually assumed that the one-electron wave functions are solutions of Schrödinger's equation for an electron in a central field, thus

$$\psi(\alpha/j) = \frac{1}{r} P(n_\alpha l_\alpha/r_j)\, S(l_\alpha m_\alpha/\theta_j \phi_j)\, \chi(s_\alpha/s_j) \qquad \ldots\ldots(3),$$

in the usual notation; P is a function of r only, S is the spherical harmonic of degree l_α, and χ is the spin wave function. P, S; l_α, χ

The analytical work of evaluating the integrals for the energies and the oscillator-strengths, with wave functions of the determinantal form (2), is greatly simplified if the one-electron wave functions are taken to be mutually orthogonal and normalized. If the form (3) is taken for the one-electron wave functions, those ψs for which l, m, or s is different are orthogonal on account of the properties of the spherical harmonics, or because of the spin functions. Those for which l, m and s are the same but n different are not orthogonal. We can, however, replace these one-electron wave functions by linear combinations which are orthogonal, and since this leaves the determinant unaltered the values of the integrals will not change. The method of constructing one-electron orthogonal wave functions out of non-orthogonal has been described by McDougall[8] and involves the radial wave functions P only.

We shall denote by P_0 the orthogonal radial wave functions obtained from the non-orthogonal self-consistent-field radial wave function P_n, and shall assume throughout the theoretical discussion that all wave functions are normalized. P_0

§ 3. FORMULA FOR THE ENERGY

The energy E of the stationary state Ψ is given by E

$$E = \int \Psi H \Psi^* d\tau \qquad \ldots\ldots(4),$$

provided

$$\int \Psi \Psi^* d\tau = 1 \qquad \ldots\ldots(5).$$

Slater[5] has given a formula for the energy. He assumes that Ψ has the determinantal form (2) and that the ψs are mutually orthogonal and of the form (3). He restricts his work in that he assumes also that all the electrons move in precisely the same field. Hartree and Black[9] removed this restriction and gave the modification of Slater's result in a form which applies to the case where the radial wave functions are obtained by the method of the self-consistent field.

Adopting Slater's notation, let us write

$I(\alpha)$ $$I(\alpha)=-\frac{1}{2}\int P_0(\alpha/r)\left[\frac{d^2}{dr^2}+\frac{2N}{r}-\frac{l_\alpha(l_\alpha+1)}{r^2}\right]P_0(\alpha/r)\,dr$$

$F_k(\alpha\beta)$ $$F_k(\alpha\beta)=\iint P_0^2(\alpha/r)\,P_0^2(\beta/r_1)\,r_a^k/r_b^{k+1}\,dr\,dr_1=\int\frac{Y_k(\alpha\alpha/r)}{r}P_0^2(\beta/r)\,dr$$

$G_k(\alpha\beta)$ $$G_k(\alpha\beta)=\iint P_0(\alpha/r)\,P_0(\beta/r)\,P_0(\alpha/r_1)\,P_0(\beta/r_1)\,r_a^k/r_b^{k+1}\,dr dr_1$$
$$=\int\frac{Y_k(\alpha\beta/r)}{r}P_0(\alpha/r)\,P_0(\beta/r)\,dr \qquad \text{.....(6),}$$

r_a, r_b where r_a and r_b are respectively the smaller and larger of r and r_1, and all the integrations are from 0 to ∞.

Then the modified form of Slater's result for the energy is

$$E=\sum_\alpha I(\alpha)+\sum'_{\alpha\beta}\sum_k a_k F_k(\alpha\beta)-\sum''_{\alpha\beta}\sum_k b_k G_k(\alpha\beta) \qquad \text{.....(7),}$$

Σ, Σ', Σ'' a_k, b_k where Σ is the sum over all electrons, Σ' over all pairs of electrons and Σ'' over pairs with parallel spins. The coefficients a_k and b_k are certain definite integrals involving spherical harmonics and have been tabulated by Slater in his paper.

McDougall[8] has applied this result to the calculation of the optical terms of an atom with one series electron. The method is to neglect the perturbation of the core of the atom by the series electron, so that we may consider the energy of the optical term λ to be the difference between the energies of the atom and of the ion. The energy E_λ of the optical term is thus given by

E_λ $$E_\lambda=I(\lambda)+\sum_\alpha J(\alpha;\lambda)-\sum_{a\,\|\,\text{spin}} K(\alpha;\lambda) \qquad \text{.....(8),}$$

where the sums are now over the core electrons only.

In order to calculate the energies of the optical terms our procedure is, therefore, first to obtain the radial wave functions P_s; then by linear combination to construct the orthogonal radial wave functions P_0; to calculate the integrals I, F and G, and finally to substitute in (8) to get the corresponding E.

We shall proceed to describe the necessary calculations for the states $(2s)$, $(2p)$, $(3p)$ and $(4p)$ of the series electron of lithium.

§ 4. THE CALCULATION OF THE ENERGIES OF THE OPTICAL TERMS OF LITHIUM

Hargreaves[7] used Hartree's method of the self-consistent field to obtain approximate radial wave functions P_s, for the series electron of lithium in the states $(2s)$, $(2p)$, $(3p)$ and $(4p)$.† The core was assumed to be unperturbed by the series electron, and accordingly the same field, namely that of the lithium ion, was used for all the states. The author has calculated the P_ss for the core electrons $(1s)^2$

† The author is indebted to Mr Hargreaves for the loan of these data.

by the same method, as these were required for the construction of the orthogonal wave functions.

The process of approximation to the self-consistent field of the $(1s)^2$ group was carried out until the maximum difference between the estimated and calculated contribution to Z† from this group was 0·008. The field for the ion was found to agree with Hargreaves's published value within a maximum difference of 0·8 per cent, whereas Wilson[10], using the variation method with a variation function containing four parameters, obtained a maximum difference of 2 per cent.

Table 1

r	$P_0(1s)$	$P_0(2s)$	$P_0(2p)$	$P_0(3p)$	$P_0(4p)$
0·0	0·0000	0·0000	0·0000	0·0000	0·0000
0·1	0·6884	0·0676	0·0028	0·0017	0·0011
0·2	1·0313	0·1012	0·0099	0·0066	0·0040
0·3	1·1670	0·1135	0·0201	0·0133	0·0079
0·4	1·1808	0·1118	0·0320	0·0192	0·0128
0·5	1·1264	0·0998	0·0465	0·0275	0·0182
0·6	1·0358	0·0769	0·0620	0·0391	0·0243
0·8	0·8190	0·0306	0·0962	0·0561	$0·0372_5$
1·0	0·6129	−0·0296	0·1317	0·0769	0·0509
1·2	0·4517	−0·0980	0·1673	0·0981	0·0631
1·4	0·3207	−0·1647	0·2059	0·1179	0·0775
1·6	0·2244	−0·2279	0·2414	$0·1365_5$	0·0894
1·8	0·1552	−0·2859	0·2747	0·1531	0·0998
2·0	0·1080	−0·3376	0·3056	0·1676	0·1085
2·4	0·0489	−0·4184	0·3574	0·1910	0·1203
2·8	0·0217	−0·4703	0·3972	0·1988	0·1238
3·2	0·0094	−0·4965	0·4230	0·1983	0·1196
3·6	0·0040	−0·5018	0·4370	0·1874	0·1076
4·0	0·0002	−0·4917	0·4403	$0·1680_5$	0·0912
5	—	−0·4260	0·4155	0·0894	0·0300
6	—	−0·3312	$0·3616_5$	−0·0052	0·0368
7	—	−0·2427	0·2979	−0·1013	0·0975
8	—	−0·1706	$0·2357_5$	−0·1844	0·1410
9	—	−0·1161	0·1811	−0·2480	0·1629
10	—	−0·0772	0·1364	−0·2913	0·1633
11	—	−0·0488	0·1010	$-0·3140_5$	0·1417
12	—	−0·0323	0·0745	−0·3200	0·1104
13	—	−0·0202	0·0554	−0·3139	0·0659
14	—	−0·0128	0·0424	−0·2965	0·0188
18	—	−0·0018	0·0078	−0·1929	0·1613
22	—	−0·0002	0·0016	−0·1003	0·2458
26	—	—	0·0003	−0·0461	0·2324
30	—	—	0·0000	−0·0192	0·1863
35	—	—	—	—	0·1149
40	—	—	—	—	0·0622
50	—	—	—	−0·0001	0·0142
60	—	—	—	—	0·0026
70	—	—	—	—	0·0004
80	—	—	—	—	0·0000

$S(1s; 2s) = 0·0837$.

† I.e. *effective nuclear charge*, or number such that the charge Ze placed at the nucleus would give the same field at the point as is actually found.

For lithium only the $(2s)$ wave function need be made orthogonal to the $(1s)$ wave function. The p functions are already orthogonal to the s functions and to each other. For the normalized functions we take†

$$\left.\begin{aligned} &P_0(1s/r) = P_s(1s/r) \\ &P_0(2s/r) = [P_s(2s/r) - S(1s;\,2s)\,P_s(1s/r)]/[1-S^2(1s;\,2s)]^{\frac{1}{2}} \\ &P_0(np/r) = P_s(np/r) \qquad (n=2,\,3,\,4) \end{aligned}\right\} \quad \ldots\ldots(9),$$

$S(1s;\,2s)$ where $$S(1s;\,2s) = \int_0^\infty P_s(1s/r).P_s(2s/r)\,dr.$$

The value $S(1s;\,2s)$ is given at the foot of the tables of P_0; see table 1.

The self-consistent and orthogonal wave functions are exhibited graphically in figure 1. It will be seen that the $(2s)$ orthogonal wave function differs considerably from the non-orthogonal wave function up to $r=2$. Beyond $r=2$ the non-orthogonal and orthogonal curves are identical. The difference between the self-consistent-field radial wave function $P_0(1s)$ and the radial wave function P_f obtained from Fock's equations, $P_f(1s)$, is too small to be shown in figure 1.

The I integrals. The radial wave functions P_s have been calculated by the method of the self-consistent field, so that they are solutions of equations of the form

$$\left\{-\frac{1}{2}\frac{d^2}{dr^2} + \frac{1}{2}\frac{l_\alpha(l_\alpha+1)}{r^2}\right\} P_s(\alpha/r) = \{v_\alpha - \tfrac{1}{2}\epsilon_\alpha\}\,P_s(\alpha/r) \qquad \ldots\ldots(10),$$

in Hartree's notation[4].

From equations (6), (9) and (10) it follows that

$$\begin{aligned} I(2s) &= \int_0^\infty P_0(2s/r)\,[(v_{2s} - 3/r - \tfrac{1}{2}\epsilon_{2s})\,P_s(2s/r) \\ &\qquad - S(2s;\,1s)\,(v_{1s} - \tfrac{1}{2}\epsilon_{1s} - 3/r)\,P_s(1s/r)]\,\frac{dr}{\{1-S^2(1s;\,2s)\}^{\frac{1}{2}}} \\ &= -\tfrac{1}{2}\epsilon_{2s} + \int_0^\infty P_0^2(2s/r)\,(v_{2s} - 3/r)\,dr \\ &\qquad + \frac{S(1s;\,2s)}{\{1-S^2(1s;\,2s)\}^{\frac{1}{2}}}\int_0^\infty \{v_{2s} - v_{1s}\}\,P_0(1s/r)\,P_0(2s/r)\,dr \qquad \ldots\ldots(11). \end{aligned}$$

Similarly, $$I(np) = -\tfrac{1}{2}\epsilon_{np} + \int_0^\infty P_0^2(np/r)\,\{v_{np} - 3/r\}\,dr \qquad (n=2,\,3,\,4).$$

Since the field for the ion was used to calculate the series-electron wave functions,

$$v_{\text{ion}} = v_{2s} = v_{np}$$

so that $$I(np) = -\tfrac{1}{2}\epsilon_{np} + \int_0^\infty P_0^2(np/r)\,\{v_{2s} - 3/r\}\,dr \qquad \ldots\ldots(12).$$

It is not necessary to calculate the individual integrals in equations (11) and (12), as the integrals occurring in the F functions may be grouped with them, and a simplification results.

† Cf. McDougall, reference (8), p. 563.

Energies of (2*s*) *and* (*np*) *states.* From equation (8)

$$E(2s) = I(2s) + 2F_0(1s, 2s) - G_0(1s, 2s)$$

$$= -\tfrac{1}{2}\epsilon_{2s} + \int_0^\infty P_0^2(2s/r)\{v_{2s} - 3/r\}\,dr + \frac{S(1s; 2s)}{\{1 - S^2(1s; 2s)\}^{\frac{1}{2}}}\int_0^\infty (v_{2s} - v_{1s})\,P_0(1s)\,P_0(2s)\,dr$$

$$+ 2\int_0^\infty \frac{Y_0(1s, 1s/r)}{r} P_0^2(2s/r)\,dr - G_0(1s, 2s) \quad \ldots\ldots(13),$$

by substitution from equations (6) and (11).

Now if an exact solution of the self-consistent field has been obtained

$$(rv_{2s}) = [Z_p]_{1\text{on}} = 2\,[Z_p]_{1s} + 1,$$

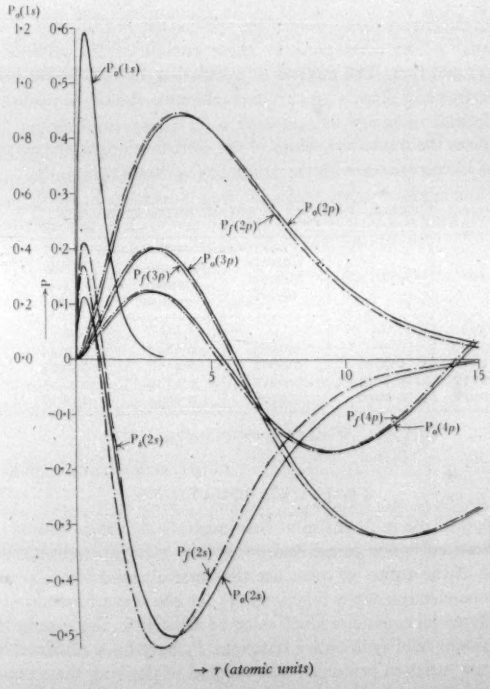

Figure 1. Normalized radial wave functions for lithium. — — — from solutions of the equations of the self-consistent field (P_s). ——— from the solutions of the self-consistent field but made orthogonal to 1*s* wave function (P_0). —·—·— from solutions of Fock's equations (P_f). The scale of the ordinate of the 1*s* radial wave function is half that of the other radial wave functions.

and $Y_0(1s, 1s/r) = 1 - [Z_s]_{1s}$,† so that

$$E(2s) = -\tfrac{1}{2}\epsilon_{2s} - \int_0^\infty \left[-\frac{S(1s;\,2s)}{\{1 - S^2(1s;\,2s)\}^{\frac{1}{2}}}(v_{2s} - v_{1s}) + \frac{Y_0(1s, 2s/r)}{r} \right] P_0(1s/r)\, P_0(2s/r)\, dr \qquad \text{.....(14).}$$

The integral in this last equation will be referred to as *the contribution to the energy* $E(2s)$.

Similarly, the integral in $I(np)$ cancels out with the contribution from the Fs, and the values of the energies are

$$E(np) = -\tfrac{1}{2}\epsilon_{np} - \tfrac{1}{2}\, G_1(1s, np),$$

where

$$G_1(1s, np) = \int_0^\infty \frac{Y_1(1s, np/r)}{r}\, P_0(1s/r)\, P_0(np/r)\, dr \qquad \text{.....(15).}$$

The ϵs are the energy parameters of the self-consistent field, and have been given by Hargreaves[7]. The corrections to these consist of the additional terms in equations (14) and (15). The method of calculating Y_0 and Y_1 has been fully described in Hartree and Black's paper[9] and reference should be made to that paper for further details.

Table 2 gives the numerical values of the contributions to the energies and the total energies in accordance with the relations (14) and (15).

Table 2. Energies of optical terms of lithium

Term	ϵ	$G_1(1s, np)$	Contributions to $2E$	$2E$ orthogonal wave functions	$2E$ Fock wave functions	$2E$ observed values
$1s$	5·570	—	—	—	—	—
$2s$	0·3560	—	0·0283	0·3843	0·3934	0·3964
$2p$	0·2518	0·0078	0·0052	0·2570	0·2574	0·2606
$3p$	0·1117	0·0023	0·0015	0·1132	0·1135	0·1145
$4p$	0·0628	0·0010	0·0006	0·0634	0·0636	0·0640

The unit of energy is e^2/a_0.

§ 5. FOCK'S EQUATIONS

The method of the self-consistent field neglects exchange effects. If we wish to include these exchange terms and so obtain a better approximation to the wave function of the atom, we must use the determinantal form (4) consisting of central-field one-electron wave functions (5) for the wave function of the whole atom. The differential equations which must be satisfied in this case by the generalized self-consistent-field radial wave functions P_l have been obtained by Fock[11], who applied the variation principle. The method of deriving these equations is to make

$$E \text{ equal to } \int \Psi H \Psi^* d\tau$$

† Cf. McDougall, reference (8), p. 573.

a minimum for small variations of the radial wave functions. The equations for sodium[12] and for lithium† have been solved numerically by Fock and Petrashen.

The Fock wave functions† are drawn in figure 1, and it is easy to see that the differences between $P_f(2s)$ and both $P_s(2s)$ and $P_0(2s)$ is considerable. The $(2s)$ wave function of the self-consistent field, $P_s(2s)$, as an approximation to the Fock $(2s)$ wave function $P_f(2s)$, is just as good as, if not better than, the orthogonal self-consistent-field wave function $P_0(2s)$. This particular property Hartree[13] found also in the case of normal beryllium. For all the series electron wave functions, the Fock wave functions are in the neighbourhood of the origin numerically greater than the corresponding self-consistent-field functions.

§ 6. FORMULA FOR THE INTENSITIES

In order to compute the intensity of the transition of the series electron from the normal state to a higher state, we require to know the value of the Heisenberg matrices,

$$R=\int \Psi^* \sum_k r_k \Psi' \, d\tau \qquad (k=1, \ldots, n) \qquad \ldots\ldots(16), \qquad R$$

where Ψ, Ψ' are the normalized wave functions of the atom in the normal and excited states respectively. Ψ, Ψ'

We shall assume that the wave function of the atom is of the determinantal form (2); that all the one-electron wave functions are orthogonal and normalized; and the approximation that raising the series electron to a higher level leaves the other one-electron wave functions unaltered. Thus, we can put

$$\Psi=\frac{1}{\sqrt{(n!)}}\begin{vmatrix} \psi(\alpha/1) & \ldots & \psi(\rho/1) \\ \vdots & & \\ \psi(\alpha/n) & \ldots & \psi(\rho/n) \end{vmatrix} \quad \text{and} \quad \Psi'=\frac{1}{\sqrt{(n!)}}\begin{vmatrix} \psi(\alpha/1) & \ldots & \psi(\rho'/1) \\ \vdots & & \\ \psi(\alpha/n) & \ldots & \psi(\rho'/n) \end{vmatrix} \qquad \ldots\ldots(17),$$

where ρ denotes the series electron which is raised to the state represented by ρ'. ρ, ρ'

The orthogonality and normalizing conditions

$$\int \psi(\lambda)\,\psi(\mu)\,d\tau=\delta_\mu{}^\lambda \qquad \lambda, \mu=\alpha, \ldots \rho, \rho' \qquad \ldots\ldots(18),$$

reduce the integral in equation (16) to

$$\frac{1}{\sqrt{(n!)}}\int \sum_k r_k \left\{\sum_P P.\psi^2(\alpha/1)\,\psi^2(\beta/2)\ldots\underset{\text{omitting } k}{\psi^2(\pi/n)}\right\}\psi(\rho/k)\,\psi(\rho'/k)\,d\tau,$$

where P denotes the permutation of the coordinates among the one-electron wave functions. P

Hence,
$$R=\frac{1}{(n!)}\int \sum_k r_k.(n-1)!\,\psi(\rho/k)\,\psi(\rho'/k)\,d\tau$$

$$=\frac{1}{n}\int \sum_k r_k\,\psi(\rho/k)\,\psi(\rho'/k)\,d\tau$$

or
$$R=\int \psi(\rho).r.\psi(\rho')\,d\tau \qquad \ldots\ldots(19),$$

† These have been taken from Fock and Petrashen's work[27]. The author wishes to express his gratitude to Miss Petrashen for allowing him to use the figures previous to their publication.

which depends only on the one-electron wave functions of the series electron which is excited. It is to be remembered that this is only true when we assume that the excitation leaves the other electrons unperturbed.

If we now replace $\psi(\rho)$ and $\psi(\rho')$ by the central-field form (5), the integrals (19) consist of three portions; two of these depend upon θ and ϕ, and can be evaluated. We are then left with a single integral which is a function of the radial wave functions only.

We obtain finally,

$$\sum_{mm'} R^2_{nlm,\,n'l'm'} = \left(\int_0^\infty rP\,(nl/r)\,P\,(n'l'/r)\,dr\right)^2 \qquad \ldots\ldots(20),$$

where the Ps are orthogonal and normalized, and (nlm), $(n'l'm')$ are the quantum numbers of the states ρ and ρ'.

The oscillator-strengths, f values, are obtained from Sugiura's formula[2],

$\nu_{nl,\,n'l'}$

$$f_{nl,\,n'l'} = \frac{1}{3}\cdot\frac{1}{g_{nl}}\cdot\frac{\nu_{nl,\,n'l'}}{R_0}\sum_{mm'} R^2_{nlm,\,n'l'm'} \qquad \ldots\ldots(21),$$

g_{nl} where $g_{nl}=(2l+1)$ and is the statistical weight of the low-energy configuration (nl) and $\nu_{nl,\,n'l'}$ the wave-number of the line corresponding to the transition (nl) to

R_0 the higher configuration $(n'l')$. R_0 is the Rydberg constant.

After we have found a central field which gives a satisfactory representation of the energy levels, we may use the radial wave functions calculated from this field to compute the radial integrals $\int rP\,(nl/r)\,P\,(n'l'/r)\,dr$. From these we can calculate the oscillator-strengths, and the ratios of the oscillator-strengths may be compared with the experimental data.

The radial integrals for lithium, for which $n=2$, $l=0$, $n'=2$, 3, 4, $l'=1$, were calculated by numerical integration and their values when P is equal to P_s, P_0, and P_f are given in table 3, together with the corresponding values of ν and f. The

ν wave-numbers ν were taken as the differences between the negative energies of the states (nl) and $(n'l')$ except for the non-orthogonal self-consistent field where

Table 3. Calculated values of the oscillator-strengths or f numbers

	$\int_0^\infty rP\,(2s/r)\,P\,(np/r)\,dr$			$\left(\int_0^\infty rP\,(2s/r)\,P\,(np/r)\,dr\right)^2$		
$2s-2p$	$-4{\cdot}49$	$-4{\cdot}515$	$-4{\cdot}135$	$20{\cdot}16$	$20{\cdot}38_5$	$17{\cdot}10$
$2s-3p$	$0{\cdot}3573$	$0{\cdot}5375$	$0{\cdot}1905$	$0{\cdot}1276$	$0{\cdot}2889$	$0{\cdot}0363$
$2s-4p$	$0{\cdot}3890$	$0{\cdot}3586$	$0{\cdot}1719$	$0{\cdot}1512$	$0{\cdot}1286$	$0{\cdot}0295_5$
	(a)	(b)	(c)	(a)	(b)	(c)

ν in atomic units				f numbers		
$0{\cdot}1042$	$0{\cdot}1273$	$0{\cdot}1360$	$0{\cdot}1358$	$0{\cdot}7000$	$0{\cdot}8650$	$0{\cdot}7751$
$0{\cdot}2443$	$0{\cdot}2711$	$0{\cdot}2799$	$0{\cdot}2819$	$0{\cdot}0104$	$0{\cdot}0261$	$0{\cdot}0034$
$0{\cdot}2932$	$0{\cdot}3209$	$0{\cdot}3298$	$0{\cdot}3324$	$0{\cdot}0147$	$0{\cdot}0137_5$	$0{\cdot}0032$
(a)	(b)	(c)	Observed	(a)	(b)	(c)

(a) Calculated from non-orthogonal radial wave functions ($P=P_s$).
(b) Calculated from orthogonal radial wave functions ($P=P_0$).
(c) Calculated from Fock radial wave functions ($P=P_f$).

they are the differences between the energy parameters ϵ. The experimental values were not used.

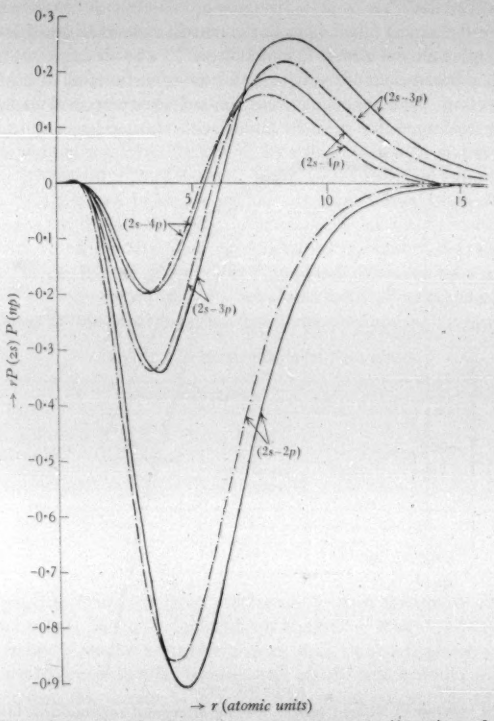

Figure 2*a*. The variation of $rP\,(2s)\,P\,(np)$. ——— for orthogonal self-consistent field radial wave functions P_0. —·—·— for Fock radial wave functions P_f.

Considerable care has to be taken in the calculation of $\int rP\,(2s/r)\,P\,(3p/r)\,dr$ and $\int rP\,(2s/r)\,P\,(4p/r)\,dr$ as the positive and negative contributions to these integrals are very nearly equal. A small change, therefore, in the wave functions has quite a large effect on the value of the integrals and correspondingly on the f numbers. Figures 2*a* and 2*b* show the variation of $rP\,(nl/r)\,P\,(n'l'/r)$ with r.

§ 7. RESULTS AND DISCUSSION

For the energy parameter for the (1*s*) state the value obtained by the author by applying the method of the self-consistent field was 5·570 in atomic units. Bethe[14] in calculating the electron distribution of Li^+ by the Hylleraas[15] or

variation method obtained 5·589, whilst the experimental value of the ionization potential of Li^+ is 5·560 according to Bacher and Goudsmit[16] and 5·564 according to Edlén and Ericson[17].

The other theoretical calculations of the normal state of Li and Li^+ are those of Eckart[18], Guillemin and Zener[19], and Wilson[10], who all employed the variation method with a determinant of the type (4) for the wave function of the whole atom. The one-electron wave functions were limited to a specified analytical form, Eckart using hydrogen-like wave functions with two parameters, Guillemin and

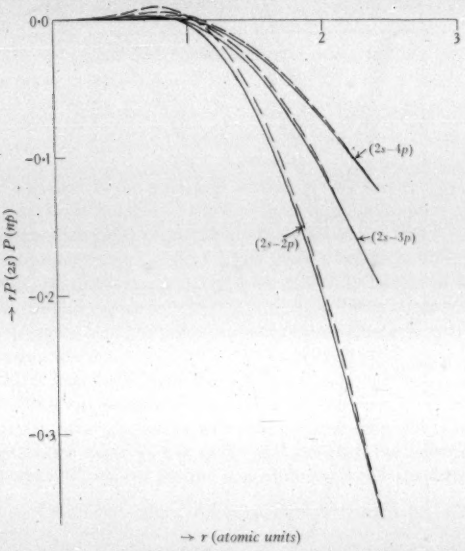

Figure 2*b*. The variation of $rP(2s)\,P(np)$. ——— for orthogonal self-consistent field radial wave functions P_0. — — — for non-orthogonal self-consistent field radial wave functions P_1.

Zener three parameters, and Wilson four parameters. Zener[20] and Slater[21] have proposed slightly simpler functions than Eckart's. The results for the energy of the (2*s*) state by these methods, as given by Wilson[10], are included in table 5. James and Coolidge[22] have recently obtained the value 0·3950 by an extended Hylleraas method.

The improvement effected in the E values over the energy parameters ϵ of the self-consistent field by the inclusion of the interchange terms of the Slater formula is very satisfactory. An even greater improvement is obtained by using the solutions of the Fock equations—see columns 2, 5, 6 and 7 of table 2. The greatest differences between the self-consistent field, orthogonal self-consistent field, Fock, and observed values of the energies are of the order of 10, 3 and 1 per cent respectively.

McDougall has pointed out[8] that the self-consistent-field wave functions for the series electron outside the core are better approximations than those obtained by making the wave functions fit the observed ϵ. It seems possible, therefore, that, since the main contributions to the *f*s come from outside the core, the *f*s calculated from wave functions made to fit the observed ϵ are the least accurate, those from the self-consistent field or orthogonal self-consistent field are more accurate, and those from the Fock equations are the most accurate.

Calculations of the *f* numbers for the first two lines of the principal series ($2s$–np) of lithium have been made by Trumpy[23] by using radial wave functions based on an empirical field of force for the atom. He obtained this field from the observed term-values by a method based on the old quantum theory (Sugiura's method). Later[24] he revised the work, using a Hartree field but one so modified that the wave functions fitted the boundary conditions for the observed ϵ. In table 4 the experimental values for the ratios of the *f* numbers, measured by Trumpy[25] and by Filippov[26], are compared with the calculated values. The calculated values are those calculated in this paper together with those obtained by Trumpy[23, 24].

Table 4. Relative values of *f* numbers

	Calculated values					Observed values	
	Self-consistent field (Hargreaves)	Orthogonal self-consistent field (author)	Fock wave functions (author)	Trumpy 1928	Trumpy 1930	Trumpy	Filippov
f_{2s-2p}/f_{2s-3p}	67·3	33·1	222	11·2	136	—	136·5
f_{2s-3p}/f_{2s-4p}	0·71	1·90	1·05	3·29	1·17	1·2	1·15
f_{2s-2p}	0·7	0·8650	0·7751	0·7230	0·7501	—	—

It appears that Trumpy's latest results are in close agreement with Filippov's experimental values, but it is doubtful, on account of what has been said above, whether Trumpy's results are more correct than those calculated in this paper. However, it seems certain that Hargreaves's result, which would make the third line stronger than the second, is in error. The radial integral ($2s$–$3p$) of the non-

Table 5. Energies of $1s$ and $2s$ states. Comparison of theoretical and observed values. (The unit of energy is $2e^2/a_0$)

$1s$-state		$2s$-state	
Energy parameter; author*	5·570	Energy parameter; Hargreaves[7]*	0·3560
Bethe[14]*	5·589	Orthogonal self-consistent field; author*	0·3843
Edlén and Ericson[17]†	5·564	Fock*	0·3934
Bacher and Goudsmit[16]†	5·560	Wilson[10]*	0·3934
		Guillemin and Zener[19]*	0·3912
		Slater[21]*	0·3906
		James and Coolidge[22]*	0·3950
		Bacher and Goudsmit[16]†	0·3964

* Theoretical value. † Observed value.

orthogonal self-consistent field is less than the radial integral ($2s$–$4p$). This does not occur in either the orthogonal self-consistent field or the Fock case; see table 4.

In conclusion, it is to be noted that for numerical in contrast to theoretical work, it is more convenient to use unnormalized wave functions (preferably those with the same dP/dr at $r=0$ for the same l) throughout, and to divide by the normalizing factors at the end of the calculations. Although all the wave functions quoted in this paper are given in the normalized form, nearly all the calculations were made with unnormalized functions, and the results were subsequently normalized by means of the appropriate factors.

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AN EXPERIMENTAL INVESTIGATION OF THE VALIDITY OF OHM'S LAW FOR METALS AT HIGH CURRENT-DENSITIES

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ABSTRACT. The paper describes experiments in which simultaneous measurements were made of the resistances of a gold conductor to a large direct current and a relatively small alternating current of radio frequency. At such frequencies the temperature of the conductor was found to remain practically constant in spite of the periodic nature of the heating effect produced by the alternating current. Thus any difference between the a.-c. and d.-c. resistances indicated a departure from Ohm's law, the skin effect being negligible. The experiments showed that the resistance of a gold conductor at constant temperature rises at very high current-densities and that the amount by which it rises increases with the temperature. The tests were made at current densities which reached 6×10^6 A./cm.^{2}

§ 1. INTRODUCTION

MANY attempts have been made[1] to establish experimentally a deviation from Ohm's law* at high current-densities but it was not until 1922, when Prof. Bridgman[2] took up the matter, that any real progress was achieved. The great difficulty in making any crucial measurements has always been to distinguish between resistance changes due to temperature and those due simply to current density.

As a result of his investigations Bridgman claimed to have observed in the case of gold a definite deviation from Ohm's law at about a million ampères per cm.^{2}, but the range of his measurements was very limited, and when in 1930 the author[3] repeated and extended Bridgman's work, introducing a number of refinements, he was driven to conclude that after the effect of heating had been properly eliminated the resistance became independent of the value of the current up to densities as high as two million A./cm.^{2}

The experiments herein described show that a deviation from Ohm's law does in fact exist at 2×10^6 A./cm.^{2}, but at ordinary temperatures it is too small to have been detected with certainty by either Bridgman's or the author's previous apparatus. The present work demonstrates clearly that the resistance of a gold conductor at constant temperature rises at very high current-densities and that the amount by which it rises increases with the temperature.

* Formulated by the Munich physicist G. S. Ohm (1787–1854).

§ 2. PRINCIPLE OF EXPERIMENT AND DISCUSSION OF PREVIOUS WORK

The method of investigation employed was similar to that originally devised by Bridgman and consists in passing simultaneously through the conductor under test a relatively large d.c. and a small a.c. The potential-difference across the conductor is balanced in a simple bridge circuit firstly with a moving-coil galvanometer and secondly with a sensitive a.-c. detector. As one would expect, the balancing resistances are normally exactly the same for the d.c. and for the a.c. provided that the frequency is not so high as to introduce disturbances due to stray inductances, capacitances, etc. If, however, the density of the d.c. is raised sufficiently, the a.-c. resistance becomes slightly larger than the corresponding d.-c. resistance, the difference becoming smaller with an increase in the frequency of the a.c.

These facts can be explained by considering the {voltage, current} curve for the conductor under test and bearing in mind that the ordinary effect of heating will be to cause the voltage to rise more rapidly than the current at large values. Thus in figure 1 the d.-c. balance gives a resistance at the point W represented by the slope of the straight line OW, whereas the a.-c. balance with a low frequency gives a resistance at the same point represented by the slope of the line MWN or of the tangent to the curve at W. It is important to remember that in the bridge circuit a balance of potentials is obtained, and the value derived for the unknown resistance is that which would give an equal potential-drop in similar circumstances.

In order to get a very high current-density without employing a large current, and at the same time providing a sufficient cooling surface, it is necessary to use a conductor of small sectional area in the form of a thin film. The temperature of such a conductor responds readily to a change in the rate at which energy is dissipated in it, so that when the a.c. superposed on the d.c. is of comparatively low frequency, causing variations to take place about the point W on the curve as shown in figure 1, the corresponding changes in p.-d. would be expected to follow the static characteristic MWN.

The higher the frequency of the a.c. the smaller the fluctuations of temperature due to it, and the observed a.-c. resistance should approach the d.-c. resistance as the frequency rises. If the upward curvature of the {voltage, current} characteristic is due only to a rise of temperature, one would naturally expect that at radio frequencies the a.-c. resistance and the d.-c. resistance would become practically equal, the skin effect being negligible for the conductor employed. At an intermediate frequency the a.-c. resistance should correspond with the slope of a line such as $M'WN'$ in figure 1.

Plotting the difference between the a.-c. and the d.-c. resistances against the reciprocal of the frequency gives the curve[3] shown in figure 2, and the effect of the periodic heating and cooling of the conductor with the a.c. can obviously be eliminated if this curve is produced to cut the axis, the point of intersection corresponding with infinite frequency. For Ohm's law to be strictly true the extra-

polation must carry the curve, figure 2, through the origin, since in that case at infinite frequency there can be no difference between the a.-c. and d.-c. resistances. This is only another way of saying that for a conductor maintained at constant temperature the {voltage, current} characteristic is a straight line through the origin. On the other hand any departure from Ohm's law will be shown by an intercept such as *OH* on the vertical co-ordinate.

Employing this method to test the validity of Ohm's law must of necessity involve a certain amount of extrapolation of the curve shown in figure 2, and therein lies the weakness of the experiment. It was precisely this weakness that led Bridgman to interpret his results for gold and silver films as showing a definite deviation from

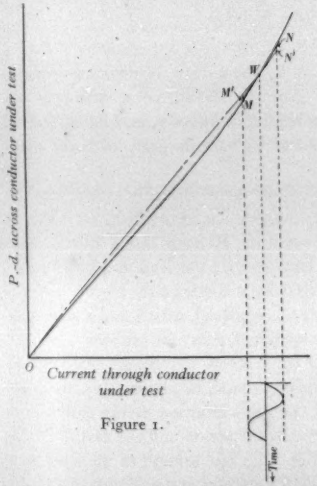

Figure 1.

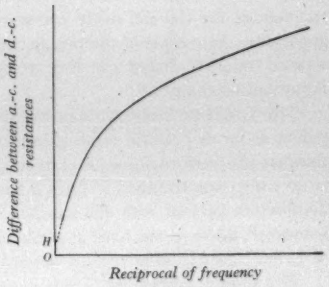

Figure 2.

Ohm's law at current-densities of the order of 10^6 A./cm.^{2} The superposed a.c. he employed was varied in frequency from 320 to 3750 c./sec., and with such low values covering so small a range it is impossible to rely with any certainty on the extrapolation process.

Realizing the importance attached to this point, the author in his previous investigation extended the frequency-range used up to 14,000 c./sec. and showed that in the case of gold at 2×10^6 A./cm.^{2} there was every indication of the difference between the a.-c. and d.-c. resistances becoming zero at an infinite frequency. There still remained, however, an element of doubt, and in order to come to a definite conclusion on this point the frequencies used in the present experiments were carried as high as $1{\cdot}15 \times 10^6$ c./sec., thus taking the measured values from which figure 2 is derived very near to the axis and reducing the extrapolation required to a minimum.

The magnitude of the a.c. passed through the conductor under test was shown previously[3] to be immaterial to the observations provided that it was small compared with the d.c. When the a.c. expressed as a fraction of the d.c. was varied from $\frac{1}{500}$ per cent up to about 0·5 per cent no measurable change occurred in the results obtained. In the present experiments the ratio adopted was between $\frac{1}{50}$ and $\frac{1}{20}$ per cent.

Both the d.c. and a.c. flow through the conductor during the measurement of the two resistances, so that no error is introduced by the slight increase in the average temperature due to the a.c.

§ 3. EXPERIMENTAL WORK

Description of apparatus. The general scheme of these experiments followed much the same lines as that previously adopted by the author, but the use of radio frequencies for the a.c. made necessary an entirely different construction of the apparatus. An outline of the bridge circuit is shown in figure 3, and figure 4 gives a more complete diagram of the arrangement of its various parts with the more important accessories.*

The balancing resistances in the bridge circuit were specially constructed to reduce as far as possible residual inductance, capacitance, skin effect, etc., and all components were enclosed in earthed metal screens. In each case a Eureka wire of 47 s.w.g. was arranged to form a narrow loop so that the lead and return conductors ran parallel with one another separated by a distance of 1 mm. The resistance P, figure 3, was fixed at a value of 42·1 Ω., whilst Q, which had a resistance of 71·8 Ω. (74·1 Ω. after reconstruction), was used as a potential-divider.

The sliding contact on Q was controlled by a screw movement as shown in figure 5. This piece of apparatus was very carefully made, to prevent any looseness between the rotary motion of the screw and the linear motion of the slider. The wire used was also selected as having a uniform cross-section and the assembly was calibrated to give a known transfer of resistance from one section of the slide wire to the other when the screw was turned through a certain angle. Thus an angular displacement of the operating handle amounting to 10 degrees corresponded with a resistance between tapping points of 0·0051 Ω. (0·00526 Ω. after reconstruction). The whole apparatus was enclosed in an earthed metal box and the conductor to the tapping point was brought out through a flexible metal tube to give the necessary freedom of motion.

A similar potential-divider was employed for the Wagner earthing-system, but in this case the slider was moved directly by hand instead of through the agency of a screw. When the bridge was balanced, the Wagner earthing-system enabled the detector points (a and b in figure 3) to be maintained at earth-potential without applying any actual earth connexion to the main circuit.

The wires joining the various components were made as short as possible, the

* Some useful hints on the construction of this radio-frequency bridge were obtained from the paper by D. W. Dye and T. Iorwerth Jones[4].

lead and return to each part of the network being kept together and jointly screened. In spite of these precautions it was found that the residual capacity was not quite balanced, and the variable air condensers C_1 and C_2 were employed to make a

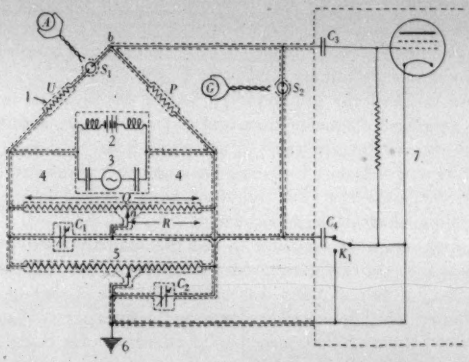

Figure 3. 1, conductor under test. 2, d.-c. supply. 3, a.-c. supply. 4, main bridge. 5, Wagner earthing system. 6, earth. 7, amplifier and detector.

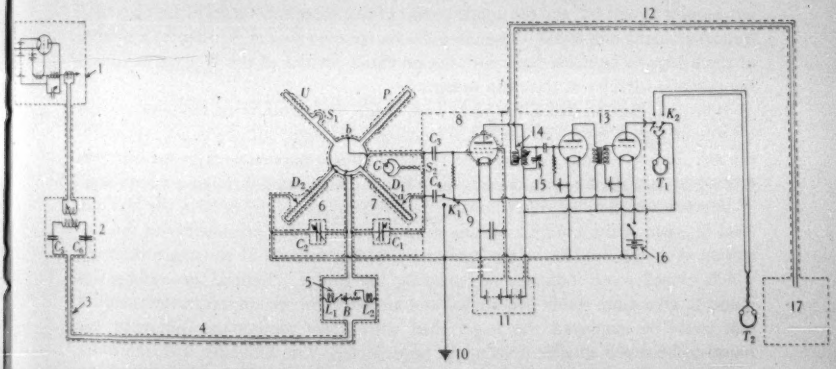

Figure 4. 1, calibrated variable frequency valve oscillator. 2, blocking condensers and coupling for h.-f. alternating current. 3, a.-c. supply to bridge. 4, 60 ft. of screened cable. 5, d.-c. supply to bridge. 6, Wagner earthing system. 7, main bridge system. 8, screen-grid h.-f. amplifier unit. 9, handle projects through screen. 10, earth. 11, S.G. and anode batteries. 12, 60 ft. of screened cable. 13, detector and l.-f. amplifier unit. 14, heterodyne input. 15, anode tuning. 16, filament battery. 17, auxiliary variable frequency valve oscillator (heterodyne).

suitable correction. A screened plug-socket S_1 was provided so that an ammeter could be connected in series with the conductor under test to measure the d.c. through it, or alternatively the socket could be short-circuited during the process of balancing the bridge.

Another plug-socket S_2 was connected to a sensitive moving-coil galvanometer to establish the condition for zero p.-d. between the detector points with d.c., and was left open-circuited when the heterodyne amplifier was employed to obtain the corresponding condition with the high-frequency a.c. The supply of current to the bridge was from an accumulator battery B feeding through choking coils L_1 and L_2 and from the calibrated variable-frequency valve oscillator O_1 coupled to the same pair of leads by means of blocking condensers C_5 and C_6.

Throughout the tests the a.c. employed was of the order of micro-amperes (about 7 μA.), ranging in frequency from 0·55 to 1·15 Mc./sec., and the balance of the bridge with this current was tested by using an auxiliary valve oscillator O_2 for heterodyning the output from a high-frequency amplifier connected to the points a, b, together with a detector, low-frequency amplifier and telephone receiver. Figure 4 shows the details of the arrangement.

The main high-frequency oscillator O_1 and the auxiliary one O_2 were situated about 60 ft. away from the bridge and from one another. To facilitate adjustment of the beat-frequency a pair of wires was taken from the output of the detector amplifier to another telephone receiver alongside the auxiliary oscillator. All parts of the equipment were carefully screened and a connexion was made to earth from the negative terminal of each filament battery.

The input to the grid of the high-frequency amplifier valve was by way of condensers C_3 and C_4, and the anode circuit of this valve was tuned to the particular frequency being employed. A single-pole change-over switch K_1 enabled a balance of the bridge to be made both with the potential-divider of the Wagner earth and the potential-divider of the main bridge.

The gold foils on which the tests were made, figure 6*a*, were mounted on the outside of a glass tube with shellac as a cement, the outer surface being exposed to the air. About midway between the terminal clips a narrow neck in the film was formed by cutting it with a razor blade while it was viewed through a microscope.

A stream of distilled water flowing transversely across the neck in the film was used in some of the tests for cooling purposes but, owing presumably to the formation of steam bubbles at the hottest point, fluctuations of resistance occurred which caused some difficulty in operating the bridge. Natural air cooling was found to give more stable conditions, and although the maximum current-density that could be employed was lower than with water cooling the difference was found to be much smaller than might be expected. The difficulty with the water was that the formation of a bubble caused a sudden rise in the temperature of the conductor approximating to the conditions prevailing when air was relied upon as the cooling medium.

In other tests a small resistance-grid made hot by a current passing through it was placed near the gold film, figure 6*b*, in order to provide supplementary heating. The film was for this purpose mounted on a quartz tube instead of a glass one.

Experiment showed that the best method of getting very high current-densities was to reduce the thickness of the foil and the width of the neck to a minimum.

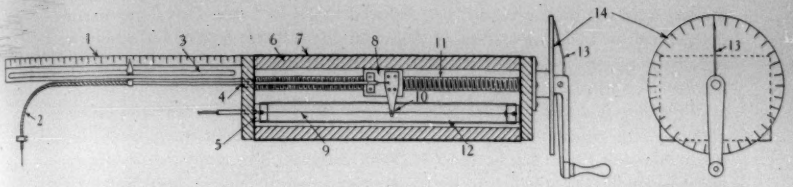

Figure 5. High-frequency potential divider for main bridge system. 1, scale. 2, screened flexible wire. 3, guide. 4, sliding fit. 5, plug to support end of glass tube. 6, wood. 7, metal screen. 8, ebonite support for slider. 9, 47 s.w.g. Eureka slide wire soldered to platinum deposited on ends of glass tube; wire returns on inside of glass tube. 10, slider. 11, screw, 26 threads per inch. 12, glass tube $\frac{3}{16}$ in. wall, $\frac{1}{8}$ in. inside diam. 13, pointer. 14, scale marked in degrees.

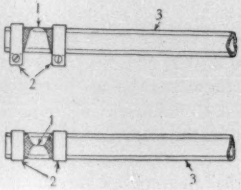

Figure 6*a*.

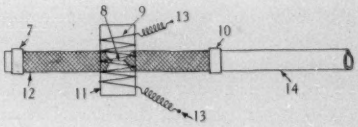

Figure 6*b*.

Figure 6*a* and *b*. Mounting for gold leaf forming conductor under test.

Figure 6*a*. Above: side elevation. Below: plan. 1, gold leaf cemented to glass tube with shellac and cut to form a narrow neck 0·5 mil. wide at this point. 2, copper clips forming terminals. 3, glass tube $\frac{9}{32}$ in. outside diam.

Figure 6*b*. 7, copper terminal clip. 8, narrow neck in gold leaf 0·5 mil. wide. 9, tungsten heater wire mounted on mica card. 10, copper terminal clip. 11, mica card. 12, gold leaf cemented to quartz tube with shellac. 13, electric heater terminals. 14, quartz tube.

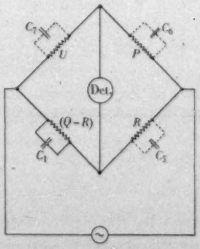

Figure 7.

The foils employed were prepared from ordinary gold leaf by continuing the beating process until the thickness had been reduced to 5×10^{-6} cm. This dimension was determined by weighing a sheet of the metal about 8 cm. square and assuming a density of 19·5 g./cm^3, a figure a little in excess of the normal, to allow for hammering. The width of the neck was measured under the microscope.

Procedure in making the measurements. The bridge, figure 4, was first balanced with a.c., the detector-amplifier and the heterodyne oscillator being used to give a suitable beat-frequency in the telephone receiver. The potential-dividers and variable condensers attached to the Wagner and main bridge systems respectively were adjusted alternately to give simultaneous balance for both positions of the switch K_1. With d.c. the condition for balance was indicated by the galvanometer G.

Theory of bridge circuit and calculations. With a small d.c. one would expect the balance of resistances in the main bridge as shown by the galvanometer and by the telephone receiver to be the same. This was in fact found to be the case with a.c. of audio frequency, but at radio frequencies the effective a.-c. resistance of the gold conductor became less than the corresponding d.-c. resistance. The difference was observed to be due mainly to stray capacities, and if these were neglected over the frequency range 0·55–1·15 Mc./sec. employed in these experiments there was always an apparent difference between the a.-c. and d.-c. resistances of the conductor under test, that difference becoming smaller as the current-density was increased.

It was found that the residual inductance of the main bridge circuit was relatively negligible and that the equivalent network could be represented with sufficient accuracy by figure 7. In terms of the symbols shown on the diagram the resistance of the conductor under test was therefore given by

$$U=\frac{P(Q-R)}{R}\left[\frac{1-\omega^2 C_5 C_7 UR}{1-\omega^2 C_1 C_6 P(Q-R)}\right]=\frac{P(Q-R)}{R}[1+x],$$

where ω is 2π times the frequency.

A bar being used to distinguish d.-c. quantities, the suffix 0 to indicate low values of current-density and the suffix h to indicate high values of current-density, then

$$\overline{U}_0=U_0 \quad \text{and} \quad x_0=\frac{Q(R_0-\overline{R}_0)}{R_0(Q-R_0)}.$$

Any deviation from Ohm's law at high current-densities can be represented by Δ, equal to $U_h-\overline{U}_h$, and hence, since both x_0 and x_h are very small compared with unity,

$$\Delta=\frac{PQ}{R_h}\left[\left(\frac{R_0-\overline{R}_0}{R_0}\right)\left(\frac{Q-R_h}{Q-R_0}\right)^2-\left(\frac{R_h-\overline{R}_h}{R_h}\right)\right].$$

The numerical values of Δ shown by the curves were calculated in each case from the above expression. Applying this theory to determine figures for C_1C_6 and C_5C_7 at different frequencies indicated that these quantities should be constant, and this conclusion was confirmed by experiment. At low current-densities the setting of C_1 remained practically unchanged.

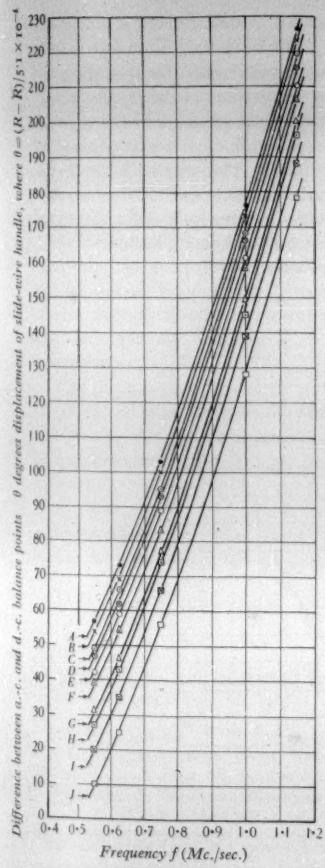

Figure 8.

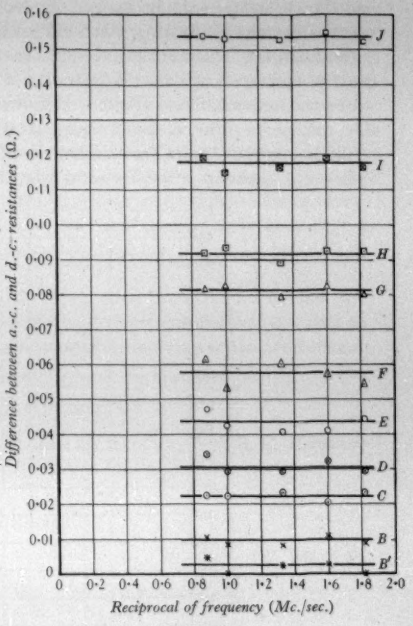

Figure 9.

Figure 8. Gold conductor, natural air cooling. *A*, $0{\cdot}24 \times 10^6$ A./cm.^{2} and $\bar{R}_0 = 23{\cdot}23\ \Omega$. *B*, $2{\cdot}44 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 23{\cdot}0\ \Omega$. *C*, $3{\cdot}23 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 22{\cdot}8\ \Omega$. *D*, $3{\cdot}58 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 22{\cdot}72\ \Omega$. *E*, $4{\cdot}02 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 22{\cdot}63\ \Omega$. *F*, $4{\cdot}41 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 22{\cdot}48\ \Omega$. *G*, $4{\cdot}96 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 22{\cdot}33\ \Omega$. *H*, $5{\cdot}2 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 22{\cdot}2\ \Omega$. *I*, $5{\cdot}67 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 21{\cdot}97\ \Omega$. *J*, $6{\cdot}15 \times 10^6$ A./cm.^{2} and $\bar{R}_h = 21{\cdot}73\ \Omega$.

Figure 9. Gold conductor, natural air cooling. *B′*, $1{\cdot}65 \times 10^6$ A./cm.^{2} *B*, $2{\cdot}44 \times 10^6$ A./cm.^{2} *C*, $3{\cdot}23 \times 10^6$ A./cm.^{2} *D*, $3{\cdot}58 \times 10^6$ A./cm.^{2} *E*, $4{\cdot}02 \times 10^6$ A./cm.^{2} *F*, $4{\cdot}41 \times 10^6$ A./cm.^{2} *G*, $4{\cdot}96 \times 10^6$ A./cm.^{2} *H*, $5{\cdot}2 \times 10^6$ A./cm.^{2} *I*, $5{\cdot}67 \times 10^6$ A./cm.^{2} *J*, $6{\cdot}15 \times 10^6$ A./cm.^{2}

Conductor 5×10^{-6} cm. thick and $1{\cdot}27 \times 10^{-3}$ cm. wide.
Bridge resistances. $P = 42{\cdot}1\ \Omega.$, $Q = 71{\cdot}8\ \Omega$.

§ 4. EXPERIMENTAL RESULTS

The family of curves shown in figure 8 shows the differences between the a.-c. and d.-c. balances of the bridge as indicated by the position of the tapping-point on the slide wire Q, figure 3, when different frequencies are employed at a given current-density. The vertical intercept between any pair of curves is practically constant and therefore almost independent of frequency. This striking fact is borne out by the curves in figure 9, where the calculated difference between the a.-c. and d.-c. resistances of the conductor under test is plotted as a function of the reciprocal of the frequency. As the lines are horizontal one can confidently assume that the values of Δ represent a true deviation from Ohm's law.

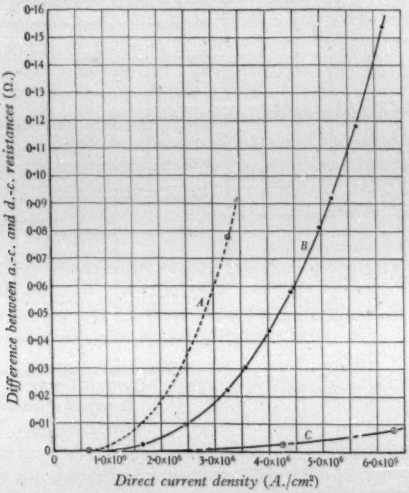

Figure 10. Gold conductor. *A*, conductor No. 2 with supplementary heating. *B*, conductor No. 1 with natural air cooling. *C*, conductor No. 1 with water cooling.

Curves similar to those shown in figures 8 and 9 were obtained when the conductor under test was cooled by a stream of distilled water flowing over it, but in this case Δ, although independent of frequency, was much smaller. Again, when the conductor under test was subjected to supplementary heating so that its temperature rose above that previously produced simply by the current through it, the difference between the a.-c. and d.-c. resistances, whilst remaining independent of frequency, became comparatively much larger.

Collected results and conclusion from experiments. In figure 10 the values of Δ signifying a true deviation from Ohm's law are plotted against current-density for different rates of cooling. The fact that the difference between the a.-c. and d.-c.

resistances is independent of frequency for radio values shows that the periodic heating and cooling effect of the a.c. has become negligible and that resistance-changes due to skin effect cannot have any material influence.

Unfortunately each curve does not represent constant temperature conditions since the rate of heating varies with the current density. Nevertheless there can be no doubt that the observed deviation from Ohm's law is a function both of current-density and of temperature. Thus one can confidently state that the resistance of a gold conductor at constant temperature rises at high current-densities, and the amount by which it rises increases with the temperature.

At low current-densities there is no deviation from Ohm's law even at comparatively high temperatures, but when the current-density is raised sufficiently for such a deviation to appear its magnitude increases rapidly with the temperature. After a certain minimum current-density has been reached there is in fact a possibility that the deviation from Ohm's law becomes entirely a function of temperature.

The present observations do not yield information from which a definite law governing the changes that take place could be deduced but the author hopes to probe further into the matter and if possible to establish an exact connexion between the quantities concerned.

§ 5. ACKNOWLEDGMENT

In conclusion the author desires to express his thanks to Prof. R. O. Kapp for placing the apparatus in the Pender Laboratory at his disposal.

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DISCUSSION

Dr D. OWEN. The subject of the paper is of great theoretical interest. In the conduction of electricity through a gas ionized at a constant rate Ohm's law fails when the current-density is sufficient to reduce appreciably the number of ions per unit volume, and saturation is reached at higher potential-gradients. Experiments on semi-insulating liquids appear to indicate a similar approach to a saturation current. The author's experimental dispositions in search for a similar effect in

metals, as described in this paper, seem admirably adapted to the purpose. An observed difference between the d.-c. resistance and the differential resistance obtained by superposition of a small alternating current should at first sight suffice to establish a departure from Ohm's law. But any alternating change of the temperature and consequently of the resistance of the conductor arising from the change in rate of evolution of heat produced by superposition of the alternating current tends to vitiate this conclusion. That such an effect is actually present in the experiments here described is suggested by the curves of figure 10, which indicate how considerable is the influence of the mode of cooling adopted. Calculation bears out the suggestion. For let I denote the large direct current, and $i_0 \sin pt$ the small superposed alternating current in the gold conductor. The increased rate of heating is $2Ii_0 \sin pt$, which will produce an oscillation of temperature of the same frequency, and consequently an addition $r_0 \sin pt$ to the resistance of the conductor. This change of resistance is doubtless very small, but it is important to note that the main current is flowing through it, with the result that virtually an e.m.f. $Ir_0 \sin pt$ is present in that arm of the bridge. The bridge is thus actually unbalanced by the very current required to supply the criterion. The d.-c. balance of course remains apparently unaffected, since the d.-c. indicator does not respond at the high frequency. The way out of this difficulty is clearly to use instead of gold a metal having a very low temperature coefficient of resistance, and it is to be hoped the author will find a means of making this step practicable.

Prof. W. Wilson suggested that the current might not be uniformly distributed in the film.

Dr L. Hartshorn. It is surprising that the author has been able to make films as thin as 0·05 μ., to weigh them, cut them to shape, and mount them on glass tubes. It would be interesting to have details of these processes. For instance, what tools are employed for the beating and subsequent manipulation? It might be worth while to make similar measurements on films prepared by sputtering, evaporation, precipitation, and electro-deposition. Probably films prepared by beating approximate more closely to the condition of metal in bulk, but it would be interesting to find out whether the observed property is characteristic of the method of preparation. If, as has been suggested, the peculiar properties of very thin films are characteristic of all surface molecules one might expect the same results with films prepared by all methods, but the question whether the property is also one of metal in bulk would still remain open. Similar experiments on films of various thicknesses might throw some light on this question.

Prof. H. Stansfield. Ohm's law may be divided into two parts: (1) the formula which Clerk Maxwell wrote $E = CR$ and described as a definition of R and (2) the information about R so defined gained from experiment, particularly as to how far R is independent of C. A President of this society who took a great interest in the history of physics, the late Prof. Sylvanus Thompson, maintained that Ohm's law would be true even if the resistance of a metallic conductor should be found to

vary with the current. I should say however that the general tendency in this country has been to move the title "Ohm's law" from (1) to (2), owing probably to the feeling that a definition should not be called a law. I incline the other way. I regard the definition as the essence of Ohm's contribution and the author's work described in this paper as a fresh tribute to its importance as well as an extension of our knowledge included in (2).

Mr R. S. WHIPPLE. Very thin films which have been chemically deposited are rarely homogeneous and may contain pin holes. I would suggest that a homogeneous film might perhaps be obtained if the author could devise a method of cathodic sputtering on to his surface, the latter being slowly rotated during the sputtering.

AUTHOR's reply. Dr Owen points out that any periodic change in the resistance of the conductor resulting from the superposed alternating current introduces a small alternating potential-difference which may invalidate the results obtained. This is undoubtedly one of the principal difficulties in connexion with the experiment, and indeed at comparatively low frequencies the heating and cooling effect referred to by Dr Owen does become one of the controlling factors. But I have shown that when the alternating current is very small and its frequency high the effect becomes negligible, as is indicated by the fact that the difference between the a.-c. and d.-c. resistances is then independent of frequency. In these circumstances the temperature of the conductor presumably remains substantially constant. Further experiments confirm this conclusion. They show that the difference between the a.-c. and d.-c. resistances becomes a function of frequency even at radio values, when the magnitude of the alternating current is sufficiently increased.

The observed departure from Ohm's law is exceedingly small and does not appear until the conductor is on the point of fusing. The figures recorded in the paper refer to a conductor having a resistance of about 96 ohms so that the largest value of Δ expressed as a percentage of this resistance is only about 0·15 per cent. Experiment indicates that the effect of temperature and method of cooling, on the value of Δ is accounted for by the change in the resistance of the conductor U and that Δ/U is independent of temperature, depending only upon the current-density. Thus a conductor of small resistance has a correspondingly small value of Δ for a given current density.

The suggestions of Dr Owen, Dr Hartshorn and Mr Whipple that similar experiments should be made on a conductor of low temperature coefficient and on films prepared by different methods are excellent ones and I hope to carry out a further investigation on those lines. In particular, graphite suggests itself as having a negative temperature coefficient and it can be readily prepared in a suitable form.

The process by which the gold conductors were made is referred to on page 556 of the paper. Raw hide was used to beat the metal down to the minimum thickness possible without destroying the continuity of the film. It was found that pure gold leaf would not stand as much beating as the gold alloy which is used commercially. This alloy was therefore employed in the experiments described. The film was

mounted on the glass by rolling the tube, made slightly sticky with a very thin layer of shellac, over the surface of the leaf. A narrow neck in the film was then formed by cutting it with a safety-razor blade, the operation being performed under a microscope. This gave an opportunity to select a homogeneous part of the film for the formation of the neck.

As regards Prof. Wilson's remark, I do not think there is any reason to expect the distribution of current in the film to vary under the conditions of the experiment.

Prof. Stansfield raises the interesting question—what is really meant by Ohm's law? My information leads me to agree with Prof. Stansfield that Ohm's contribution consisted in giving an accurate definition of the terms electromotive-force, current and resistance by introducing the relationship $I=E/R$. Ohm was guided in the mathematical work from which he originally deduced his famous "law" by analogy with the problem of heat-conduction, but he afterwards verified his theoretical conclusions by making a number of experiments with thermoelectric piles and observing the potential-differences between different points in an electric circuit. Later Davy, Pouillet, Becquerel, Kohlrausch, Gaugain and Branly all laboured at experimental investigations of Ohm's relationship, establishing so much confidence in its accuracy that it came to be regarded as a law of nature.

535·338.4:546.28

ULTRA-VIOLET BAND-SYSTEMS OF SiCl

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ABSTRACT. The emission spectrum of SiCl, produced in a tube discharge through a continuous flow of $SiCl_4$ vapour, has three systems of doublet bands degraded towards the further ultra-violet, the 0, 0 bands being at λλ 2942, 2924, λλ 2436, 2424, and λλ 2232, 2221. They are attributed to transitions B → X, C → X and D → X, where X is a double level with electronic separation 207·9 cm^{-1}, $\omega_e = 531{\cdot}0$ and $x_e\omega_e = 2{\cdot}2$; B is a single level 34186·0 cm^{-1} above X with $\omega_{\frac{1}{2}} = 698{\cdot}7$; C is a close doublet 41234·8 and 41247·8 cm^{-1} above X with $\omega_e = 674{\cdot}2$ and $x_e\omega_e = 2{\cdot}2$; and D is a single level 45005·9 cm^{-1} above X, with $\omega_{\frac{1}{2}} = 663$. These figures are from band-head measurements only. Datta's analysis of the B → X system is confirmed, except in his identification of the 2,0 and 3,0 bands and his interpretation of observed isotope band-heads. With Datta's 2,0 and 3,0 bands are two groups of prominent bands between λ 2830 and λ 2770 not fitting into any of the three systems; their emitter may be a chloride of silicon other than SiCl.

§ 1. INTRODUCTION

Apart of the spectrum described in this paper was observed in 1913 in the glow produced by the interaction of $SiCl_4$ vapour and active nitrogen[1]. The whole of it was observed in 1923 in the uncondensed induction-coil discharge in $SiCl_4$ vapour flowing continuously through a discharge tube[2]. Low-dispersion spectrograms of the discharge were taken with a small quartz-prism instrument (Hilger's E 6) and some of the stronger bands were also photographed in higher dispersion (about 7·5 A./mm.) with a 2·4-m. concave grating. The spectrum was seen to consist of two somewhat similar parts A and B, one on either side of the AlCl band-system that resulted from the use of aluminium electrodes. Each part consisted of bands degraded to the further ultra-violet, i.e. opposite in direction to the SiO bands, which were present if residual air had not been entirely displaced by the $SiCl_4$ vapour. Parts A and B were regarded as two related band-systems, each having progressions of bands with common separations of about 525 cm^{-1} and regular variations of intensity. A constant separation, amounting to about 205 cm^{-1} in A and 195 cm^{-1} in B, was also recognized, but this did not suffice for the make-up of the usual Deslandres' arrangement of the band-heads; it was, in fact, the interval between the heads of sub-bands such as had been observed in other doublet band-systems but were not understood. The observed numerical relations have now proved to be significant for the vibrational analysis, which was not apparent at that time.

More recently A. C. Datta[3], using a 12,000-V. discharge through $SiCl_4$ vapour at about 2 mm. of mercury and a spectrograph of much bigger dispersion (Hilger's E 1), has shown that the stronger part A between λλ 3118 and 2772 does, indeed, consist of a doublet system in which the above 205 $cm.^{-1}$ represents an electronic separation—whether it is in the upper or in the lower state is undetermined—and the intervals of about 525 $cm.^{-1}$ pertain to the vibrational levels of the lower state, the upper state having a previously unrecognized interval of nearly 700 $cm.^{-1}$ Datta also observed that the sub-bands are themselves double-headed, with a separation of from 5 to 8 $cm.^{-1}$ between the heads P_1 and Q_1 in the lower-ν sub-band, and between P_2 and Q_2 in the higher-ν.* There are band-heads in this region, some of them very intense, which are not mentioned by Datta and cannot be included in his band-system; these will be discussed presently (p. 571). The analysis of the weaker part B between λλ 2600 and 2200 is recorded in the present paper. As will appear presently, part B consists, not of one system as previously supposed, but of two systems with the same lower state as the stronger system (or systems) forming part A. Although the common lower state cannot, from emission observations alone, be identified with the ground state, it will be denoted by X for the present, and the three systems (excluding the strong bands in part A mentioned above) will be referred to as the λ 2942 or B → X,† the λ 2436 or C → X and the λ 2232 or D → X systems; these wave-lengths apply to the least refrangible heads of the three 0,0 bands.

§ 2. EXPERIMENTAL

For the new observations an uncondensed discharge through continuously flowing $SiCl_4$ vapour has again been used; it is much more powerful than was possible on the former occasion[2]. The discharge tube is a suitably modified form of the water-cooled pyrex tubes used for other purposes by Dr R. W. B. Pearse and his collaborators in this laboratory. Its essential feature is the large cylindrical sheet electrodes whose outer surfaces are in contact over their whole area with the cylindrical walls of the water-cooled glass bulbs; the only parts of the tube not wholly immersed in a tank of running cold water are the extension carrying the quartz window, through which the column is viewed end-on, and the leads to the electrodes. For the electrodes and leads nickel is used in preference to aluminium in the present case in order to eliminate the AlCl band-system[2,6] mentioned above. The $SiCl_4$ vapour is admitted into one bulb, and the gaseous products of its decomposition in the discharge are pumped away from the other, each bulb having a side tube (with stop-cock) protruding vertically above the water for this purpose. A series of soda-lime tubes protects the oil pump, which runs throughout each

* It is convenient to retain Datta's empirical designations of the heads; they have no connexion with Mulliken's use of these symbols for the theoretical classification of the branches. The rest of the notation used in the present paper is that of this Society's *Report*[4].

† Dr Sponer in tabulating Datta's results for the λ 2942 system in the first volume of her recent book[5] also denotes the lower state by X and the upper state by B. The common lower state of a number of systems observed only in emission is now so often denoted by X in the literature, that it would be well to substitute another letter G for states which are *known*, either from absorption observations or from theoretical considerations, to be ground states.

exposure. The discharge carries a 50-c./sec. current of 0·25–0·4 A. from a 5-kW. 2400-V. transformer whose primary is supplied from 230-V. mains, a suitable resistance being inserted in each circuit. With a spectrograph similar to that used by Datta, whose exposure times were about 8 hours, this discharge requires only 1½–2½ hours according to the spectral region to be measured. This instrument (Hilger's E 1) has been used for the λ 2942 system (dispersion 5·1–3·8 A./mm. in this region) and for the λ 2436 system (dispersion 3·1–2·1 A./mm.). In the latter case, since the bands are so far resolved into rotational structure as to cause uncertainty in the identification of some of the band-heads, a smaller quartz-prism instrument (a predecessor of Hilger's E 2, dispersion about 10–7 A./mm.) has also been used. Only the latter instrument has been used for the weakest system λ 2232 (dispersion 6·7–5·5 A./mm.). The plates used were Imperial Ordinary (some paraffined, some not), Ilford Ultra-violet (Q) and Eastman Ultra-violet.

As will be seen in figure 1, the present spectrograms show very little but the bands of SiCl and lines of Si, Ni and Cu.* The last-named, arising from impurity in the nickel electrodes, have been used as standards for wave-length measurement in parts of a spectrogram where the overlaps with the juxtaposed Fe arc standards happened to be not entirely satisfactory. The strongest bands of the SiO systems[2,4,8] are present but not troublesome. The N_2 Second Positive bands, three of which at λ 2976·7 (2, 0), λ 2962·1 (3, 1) and λ 2953·3 (4, 2) are the most prominent features of the spectrogram reproduced in Datta's paper, are not detectable in the present plates.

§ 3. ANALYSIS OF THE THREE SYSTEMS OF $^{28}Si^{35}Cl$

Results of measurements of band-heads in several spectrograms are set out for the three systems of the main molecule $^{28}Si^{35}Cl$ in table 1 with rough visual estimates of the relative intensities of the bands and the assigned values of the vibrational quantum numbers; the symbols used for naming the heads are those already allotted, in the λ 2942 system, by Datta, whose analysis of this system is substantially confirmed. The present observations yield, on the whole, slightly smaller and steadier values for the intervals Q_2–P_2, Q_1–P_1, P_2–P_1, and, like the rougher 1923 measurements[2], include a few more bands, some of which will be discussed presently (p. 571).

Table 2, which is a composite Deslandres arrangement of the wave-numbers of, and intervals between, the P_1 and P_2 heads, shows that the intervals in the v'' progressions are so nearly alike for the three systems as to suggest a common lower level. Denoting this by X and the upper levels by B, C and D, and accepting for the moment Datta's identification of the 2,0 and 3,0 band-heads in the λ 2942

* The presence of copper became very clear through the development of a blue glow, which was confined to edges of the electrodes when the tube was first used but almost filled the same tube when the discharge was passed after about a fortnight's disuse of the tube. The spectrum of the blue glow was photographed in about 8 minutes' exposure in the first order of a 2·4-m. concave grating (the grating mentioned on p. 563 in a newly-built Eagle mounting). It shows the stronger parts of the band-systems of CuCl[7,4] in considerable intensity.

Table 1. Data for band-heads of $^{28}Si^{35}Cl$

λ 2942 system, B $\rightarrow$ X; and other bands (p. 571)							
Intensity	v', v''	Band-head	Datta		Author		
			λ (air)	ν (vac.)	λ (air)	ν (vac.)	$\nu_{obs.} - \nu_{calc.}$
1	1, 5	P_1			3117·82	32064·4	−1·4
		Q_1			7·40	68·7	
0?	1, 5	P_2			3097·55	32274·2	+0·5
		Q_2			—	—	
2	0, 3	P_1	3085·56	32399·6	3085·61	32399·1	+1·8
		Q_1	—	—	5·13	404·2	
2*	1, 4	P_1			3068·75	32577·1	−2·1
		Q_1			7·97	85·4	
3	0, 3	P_2	3065·61	32609·5	3065·77	32608·8	+2·6
		Q_2	—	—	—	—	
2	1, 4	P_2			3049·26	32785·3	−1·8
		Q_2			8·78	90·5	
4	0, 2	P_1	3036·64	32921·9	3036·57	32922·3	+1·8
		Q_1	5·88	29·8	6·21	26·2	
6	1, 3	P_1	3020·54	33097·5	3020·51	33097·4	+0·4
		Q_1	19·90	104·1	0·08	102·1	
6	0, 2	P_2	3017·76	33127·5	3017·65	33128·7	+0·3
		Q_2	7·12	34·5	7·24	33·2	
4	1, 3	P_2	3001·62	33306·0	3001·73	33304·4	−0·5
		Q_2	1·14	10·9	1·19	10·4	
8	0, 1	P_1	2988·90	33447·4	2988·82	33448·3	+1·2
		Q_1	8·33	53·8	8·29	54·2	
4†	1, 2	P_1			2973·5	33621	+2
		Q_1			—	—	
8	0, 1	P_2	2970·30	33656·8	2970·38	33655·9	+0·9
		Q_2	—	—	0·02	60·0	
3†	1, 2	P_2			2955·0	33831	+4
		Q_2			—	—	
8	0, 0	P_1	2942·30	33977·1	2942·19	33978·4	+0·3
		Q_1	1·73	83·7	1·67	84·4	
8	0, 0	P_2	2924·41	34185·0	2924·38	34185·3	−0·7
		Q_2	3·86	91·4	3·92	90·7	
8	1, 0	P_1	2883·00	34675·8	2882·92	34676·9	+0·1
		Q_1	2·37	83·6	2·37	83·5	
8	1, 0	P_2	2865·90	34882·8	2865·80	34884·1	−0·6
		Q_2	5·33	89·8	5·28	90·4	
10‡					2829·25	35334·7	
5					8·55	42·1	
7‡§	2, 0	P_1	2826·30	35371·6	2826·15	35373·4	+0·7
		Q_1	—	—	—	—	
6					2823·56	35405·9	
8‡					2812·81	35541·2	
					2·40	46·4	
10‡§	2, 0	P_2	2809·79	35579·4	2809·70	35580·5	−0·1
		Q_2	9·15	87·5	9·19	87·0	
10					2807·18	35612·5	
4					2788·27	35854·0	
4					87·01	870·2	
6					83·63	913·7	
7§	3, 0	P_1	2771·9	36065·1	2772·00	36064·4	−1·4
		Q_1	—	—	—	—	

Table 1 (*cont.*)

v', v''	Band-head	λ 2436 system, C → X				λ 2232 system, D → X			
		Int.	λ (air)	ν (vac.)	$\nu_{obs.}-\nu_{calc.}$	Int.	λ (air)	ν (vac.)	$\nu_{obs.}-\nu_{calc.}$
1, 7	P_1	00?	2625·07	38082·9	− 2·2				
0, 6	P_2	0?	23·05	112·2	− 2·6				
0, 5	P_1	1	01·51	427·7	− 1·2				
0, 5	P_2	1	2588·31	623·8	0·0				
0, 4	P_1	1	67·27	940·2	− 2·1	0	2341·13	42701·3	+0·8
1, 5	P_1	1‖	57·5	39089	−10				
0, 4	P_2	2	54·52	134·6	− 2·6				
1, 5	P_2	1	44·30	291·7	− 1·8				
0, 3	P_1	4	33·45	460·0	− 0·1	1	2313·10	43218·7	+0·5
0, 3	P_2	1	21·02	654·6	− 0·4				
0, 2	P_1	4	00·30	983·1	+ 0·8	2	2285·53	740·0	−0·4
0, 2	P_2	6	2488·21	40177·4	+ 0·2	2	74·71	948·0	−0·3
0, 1	P_1	6	67·77	510·2	+ 1·3	5	58·38	44265·8	−1·2
0, 1	P_2	7	56·03	703·8	0·0	5	47·75	475·1	+0·2
0, 0	P_1	¶	[35·91	41039·9	0·0]	4	31·53	798·3	+0·3
1, 1	P_1	2	27·68	179·1	+ 0·4				
0, 0	P_2	3	24·39	235·0	+ 0·2	4	21·24	45005·8	−0·1
1, 1	P_2	2	16·16	375·4	+ 1·8				
1, 0	P_1	6	2396·73	710·8	+ 1·1	1?	2198·9	45461	
1, 0	P_2	5	85·58	905·7	+ 1·1				
2, 0	P_1	1	59·10	42376·1	+ 1·0				
2, 0	P_2	0‖	48·6	566	− 4				

? Rather doubtful head.

* Band certainly present but head difficult to locate exactly.

† Datta's spectrogram[3] shows these heads well separated from, and on the short-λ side of, the N_2 second positive bands at λλ 2977 and 2962, but they are not marked by symbols or λ values. They are easily visible in the enlarged print from which figure 1 has been made. The heads are very difficult to locate and their assignment to the 1, 2 band is tentative.

‡ Sharp or line-like head, or strong line superposed on head.

§ Although these heads occur near the positions expected for the 2, 0 and 3, 0 band-heads, they probably do not belong to this system. All the data below the horizontal line in table 1 are for bands which may be due to a chloride of silicon other than SiCl (see p. 571).

‖ Measured only in low-dispersion spectrograms. Very rough data taken from earlier paper[2].

¶ Sub-band present but head too near to strong Si line λ 2435·159 for reliable measurement. Roughly measured in earlier low-dispersion plates[2] as λ 2436·2, ν 41035. Values of λ and ν from equation inserted here.

system, we may roughly represent the band-head wave-numbers by the following equations:

λ 2232 system, D → X,

$$\nu = \begin{Bmatrix} 44941{\cdot}5 \\ 44733{\cdot}6 \end{Bmatrix} + (663u') - (535{\cdot}4u'' - 2{\cdot}20u''^2),$$

λ 2436 system, C → X,

$$\nu = \begin{Bmatrix} 41165{\cdot}4 \\ 40970{\cdot}5 \end{Bmatrix} + (674{\cdot}2u' - 2{\cdot}20u'^2) - (535{\cdot}4u'' - 2{\cdot}20u''^2),$$

λ 2942 system, B → X,

$$\nu = \begin{Bmatrix} 34102{\cdot}7 \\ 33894{\cdot}8 \end{Bmatrix} + (701{\cdot}5u' - 1{\cdot}40u'^2) - (535{\cdot}4u'' - 2{\cdot}20u''^2),$$

where $u' = v' + \frac{1}{2}$, $u'' = v'' + \frac{1}{2}$, and the independent coefficients roughly locate the system-origins; the residuals, $\nu_{obs.} - \nu_{calc.}$, are included in table 1. The next

Table 2.** Deslandres arrangements of wave-numbers of P_1 and P_2 heads

v'	v'' → 0	1	2	3	4	5	6	7
	(D)					λ 2232 system		
1	—							
	45461 ?							
	—							
	663?							
0	45005·8 (5307)	44475·1 (5277)	43948·0					
	207·5	209·3	208·0					
	44798·3 (5325)	44265·8 (5258)	43740·0 (5213)	43218·7 (5174)	42701·3			(X)
	(C)					λ 2436 system		
2	42566‖							
	190							
	42376·1							
	660							
	663·3							
1	41905·7 (5303)	41375·4				39291·7		—
	194·9	196·3				202·7		
	41710·8 (5317)	41179·1				39089‖		38082·9?
	670·7	671·6				667·9		
	[670·9]	668·9				661·3		
0	41235·0 (5312)	40703·8 (5264)	40177·4 (5228)	39654·6 (5200)	39134·6	38623·8 (5108)	38112·2? (5116)	
	[195·1]	193·6	194·3	194·6	194·4	196·1		
	[41039·9] ¶ (5209?)	40510·2 (5271)	39983·1 (5231)	39460·0 (5198)	38940·2	38427·7 (5125)	(5119)	(X)
	(B)					λ 2942 system		
?3	—							
	36064·4§							
	—							
	691·0							
	35580·5§‡							
?2	207·1							
	35373·4§‡							
	696·4							
	696·5							
1	34884·1		33832·1† (5277)	33304·4 (5191)	32785·3	32274·2?		
	207·2		206·5	207·0	208·2	209·8		
	34676·9		33625·6† (5282)	33097·4 (5203)	32577·1* (5127)	32064·4 (5119)		
	698·8		703·4	695·6				
	698·5		703·3	698·3				
0	34185·3 (5294)	33655·9 (5272)	33128·7 (5199)	32608·8				
	206·9	207·6	206·4	209·7				
↑	33978·4 (5303)	33448·3 (5260)	32922·3 (5232)	32399·1				(X)
v'								

** See footnotes to table 1.

fact to be noticed in table 2 is that the interval P_2–P_1 is about the same for the B → X and D → X systems but certainly less for the C → X system, the mean values used in the derivation of the equations being 207·9 and 194·9 cm.$^{-1}$* It

* The 1923 low-dispersion measurements[2] sufficed to show the reality of this difference, the mean intervals being then estimated as 205 and 195 cm.$^{-1}$.

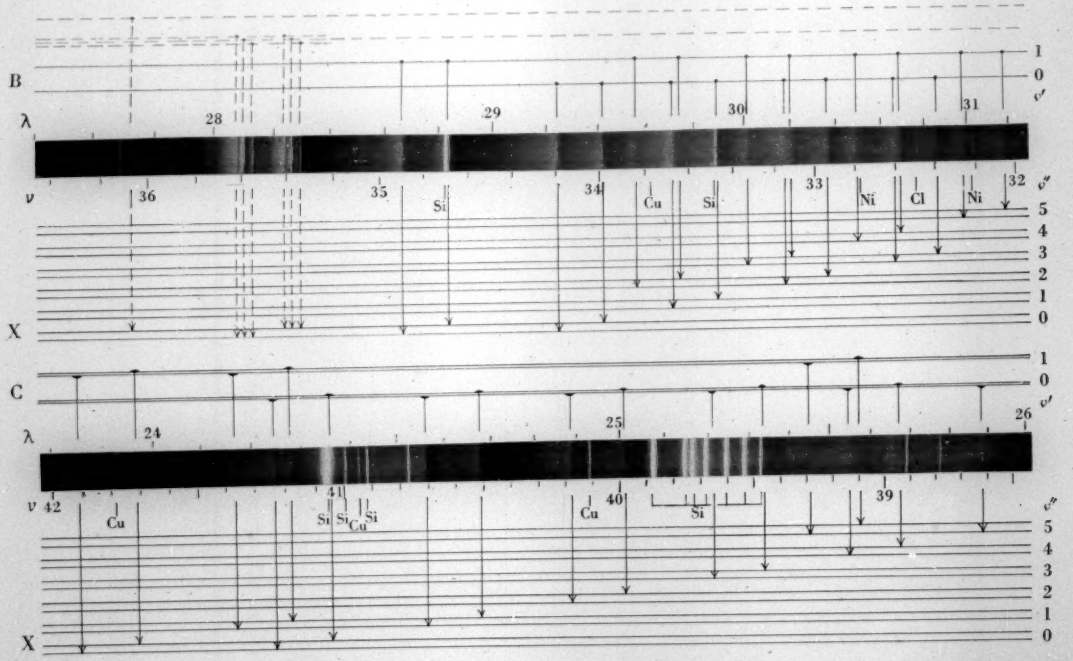

Figure 1. Two of the band-systems of SiCl and other bands (λλ 2829–2770).

To face page 568

must also be noted that the sub-bands in the C → X and D → X systems are not observed to be double-headed as are those in the B → X system; in the case of D → X this may be entirely due to the use of lower dispersion; but in the case of C → X, for which the dispersion was even higher than for B → X, it seems to indicate that the bands differ in type from those of B → X.

As to the electronic separations in the states X, B, C, D, the likeliest of the three alternative assumptions possible is that made in the construction of the energy-level diagrams in figure 1 and figure 2, namely that X has the observed separation 207·9 cm.$^{-1}$, B and D are single, and the observed difference 207·9–194·9 cm.$^{-1}$ is the electronic separation in C;* in its favour is the fact that in no other way can one avoid giving the same electronic separation to two different doublet levels. With this assumption, numerical data for the four states, so far as they can be derived from the band-head measurements, may be summarized as in table 3.

Table 3. Electronic levels and vibrational constants

State	Height of $v=0$ level above that of X_1 (cm.$^{-1}$)	Vibrational constants (cm.$^{-1}$) ω_e	$\omega_e - \frac{1}{2}$	$x_e\omega_e$
D	45005·9		663 ?	
C $\begin{cases} C_2 \\ C_1 \end{cases}$	41247·8 41234·8	674·2	669·8	2·20
B	34186·0	701·5?	698·7	1·40?
X $\begin{cases} X_2 \\ X_1 \end{cases}$	207·9 0	535·4	531·0	2·20

Comparison with results of analysis of band-systems of other halides of the same sub-group affords little or no guidance to a classification of the levels X, B, C, D. Only SnCl, which emits two ultra-violet band-systems, $^2\Sigma \rightarrow {}^2\Pi$ and $^2\Delta \rightarrow {}^2\Pi$[9, 4], has electronic levels at all resembling those of SiCl. The disposition of its $^2\Pi$, $^2\Delta$ and $^2\Sigma$ is similar to that of X, C and D of SiCl, and its electronic doublets are, as they should be, wider than those of SiCl; this is shown on the right-hand side of figure 2. If these are corresponding levels in the two molecules, B may be another $^2\Sigma$; it must be noted, however, that an SnCl system corresponding to B → X has not been found although it would be expected to be strong and well situated for observation. That X, B, C, D may be $^2\Pi$, $^2\Sigma$, $^2\Delta$, $^2\Sigma$ is no more than a suggestion. Whether the first of these is the ground state of SiCl and of SnCl can only be settled satisfactorily by observations of the band-systems in absorption. A $^2\Pi$ ground state may, as Morgan[10] points out, be expected from the atomic ground states, namely $ns^2\,np^2\,{}^3P$ with $n=2, 3, 4, 5, 6$ for C, Si, Ge, Sn, Pb respectively, and $ns^2\,np^5\,{}^2P_{1nv}$ with $n=2, 3, 4, 5$ for F, Cl, Br, I respectively. Unlike the emission systems of SiCl and SnCl, the single absorption system of red-degraded

* The other two, and less likely, alternatives are: (i) X single, and B, C and D double, the electronic separations being 207·9 cm.$^{-1}$ in B and D and 194·9 cm.$^{-1}$ in C. Dr Sponer[5] in tabulating Datta's results for the λ 2942 system tentatively adopts this alternative. (ii) C single, and X, B and D double, with separations 194·9 cm.$^{-1}$ in X and 13·0 cm.$^{-1}$ in B and D.

visible absorption bands* recently observed by Morgan for each of the molecules PbF, PbCl and PbBr is of a type which does not immediately suggest a $^2\Pi$ ground state, but may yet be, as Morgan says, the stronger and higher-ν sub-system of, say, a complete $^2\Sigma \rightarrow {}^2\Pi$, the undetected weaker and lower-ν sub-system being in the extreme red and near infra-red, since the $^2\Pi$ separation is expected to be of the order 7000 cm.$^{-1}$ in PbCl. For SiF Johnson and Jenkins[11] observed several band-systems, two of which were assigned to transitions to a common lower level X from levels α_1, α_2 and β respectively 22724, 22880 and 34561 cm.$^{-1}$ above it, $\alpha_1\alpha_2$ being a doublet ($\Delta\nu = 156$)[4]; since Badger and Blair[12] have recently reported that the

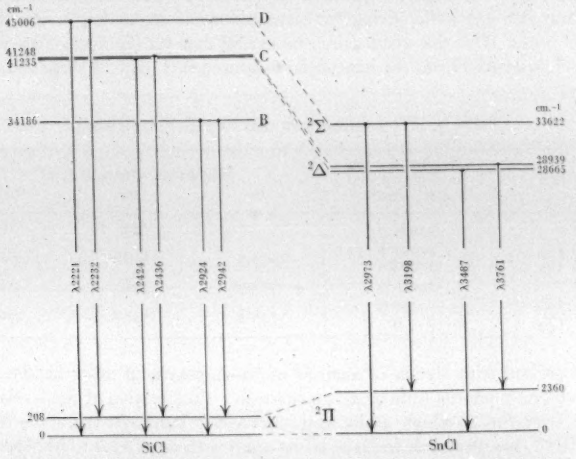

Figure 2. Electronic energy levels and band-systems of SiCl and SnCl. The widths of the double levels are exaggerated, about tenfold in SiCl and twofold in SnCl.

$\alpha_2 \rightarrow$ X bands, λ 4368, etc., are themselves double, the level X may prove to be a close doublet. For SiBr Miescher[13] has found at $\lambda\lambda$ 3233·6–2874·9 a system of emission bands whose heads are apparently single and are represented by

$$\nu = 33570 + (578{\cdot}3u' - 4{\cdot}3u'^2) - (424{\cdot}6u'' - 1{\cdot}3u''^2);$$

both of its electronic levels are single and may be $^2\Sigma$. Further observations of several halides of this sub-group, both in emission and in absorption, are much to be desired, and will, it is hoped, be undertaken as the necessary materials become available.

* *Note added March* 6: The author regrets having overlooked Rochester's recent paper[14] which records the observations and analysis of the PbF and PbCl band-systems, the former in emission and the latter in emission and absorption. It appeared simultaneously with Morgan's paper[10] and the results of the two independent investigations are in agreement. Rochester points out that Popov and Neujmin's previous analysis of PbCl fluorescence[15] is incorrect.

§ 4. OTHER BANDS

Strong bands between λ 2770 *and* λ 2830. Attention must now be directed to the bands which Datta identified as the 2,0 and 3,0 bands of the λ 2942 system. As will be seen in the plate, each sub-band of the former is the middle member of a prominent trio whose appearance is in striking contrast to that of other sub-bands in the system, their heads being very sharp or line-like and almost, if not quite, as intense as any in the system. These six heads between λ 2829·2 and λ 2807·2 occur both in the present plates of the discharge with nickel electrodes and also in the writer's 1923 plates of the discharge with aluminium electrodes and very much smaller currents; indeed, they are amongst the strong bands which, as mentioned in the opening paragraph of this paper, were measured in the first order of the 2·4-m. grating in 1923. They evidently belong to a chloride of silicon or of an impurity common to the aluminium and the nickel; their intensity suggests the former. They make up three pairs with the same, or nearly the same, separation as that already assigned to state X of SiCl, namely 207·9 $cm.^{-1}$, and would therefore appear to belong to SiCl, though not to any of the three systems described above. If this is so they require three upper levels, as indicated in broken lines in the upper left-hand corner of figure 1, with separations of about 39·0 and 32·2 $cm.^{-1}$; as the bands degrade towards the further ultra-violet these closely-spaced levels cannot, of course, be three consecutive vibrational levels of one electronic state. Against SiCl as their emitter, however, is the fact that these bands, unlike the accepted SiCl bands, show no trace of resolution into line structure. Datta makes no mention of these sub-bands, except the pair which he ascribes to the 2,0 band, although they are clearly seen in his published spectrogram[3]. The appearance of the group is, it is true, not quite the same in Datta's and the writer's plates, but this is chiefly because the former also shows with fair intensity the intervening N_2 "Second Positive" bands λ 2819·6 (3,0) and λ 2813·8 (4,1), of which there is no trace in the present plates. In the neighbourhood of Datta's 3,0 band there are, as may be seen in figure 1, also bands which do not fit into one of the above systems; unlike the former set these show some resolution into line structure. Measurements of these unallocated heads in both regions are included in the first section of table 1.

The writer is not convinced that the 2,0 and 3,0 bands of the λ 2942 system have been correctly identified, and has therefore used broken-lines for the parts of figure 1 which are in question. Without these bands the coefficients of u' and u'^2 in the equation for this system on p. 567, are not calculable; the values of ω_e and $x_e\omega_e$ for state B in table 3 are therefore queried.

Chlorine isotope effect. The abundance ratios of isotopes of Cl and Si are

$$^{35}Cl : {}^{37}Cl = 100 : 31{\cdot}4 \quad \text{and} \quad {}^{28}Si : {}^{29}Si : {}^{30}Si = 100 : 6{\cdot}95 : 4{\cdot}70,$$

and those of the only SiCl molecules that need be considered here are therefore $^{28}Si^{35}Cl : {}^{28}Si^{37}Cl : {}^{29}Si^{35}Cl = 100 : 31{\cdot}4 : 6{\cdot}95$. In the combined spectrum, then, the bands of the isotopic molecules $^{28}Si^{37}Cl$ and $^{29}Si^{35}Cl$ will have about 31 and 7 per cent, respectively, of the intensity of the corresponding bands of the main

molecule $^{28}Si^{35}Cl$. Their displacement coefficients $\rho - 1$ are not very different from one another, being $-0{\cdot}0122$ and $-0{\cdot}00967$ respectively. The band-heads of $^{28}Si^{37}Cl$ are therefore to be sought first; if they are not identified it will obviously be wrong to attribute any observed band-heads to the still rarer molecule $^{29}Si^{33}Cl$, whose bands should be only 7/31 as strong. Datta evidently overlooked this in attributing eight observed heads to $^{28}Si^{37}Cl$ and four others to $^{29}Si^{35}Cl$, the only apparent reason being that the observed displacements $\nu' - \nu$ of these four from the corresponding main $^{28}Si^{35}Cl$ heads agreed better with the calculated displacements for $^{29}Si^{35}Cl$, $-0{\cdot}00967\ (\nu - \nu_e)$, than with those calculated for $^{28}Si^{37}Cl$, $-0{\cdot}0122\ (\nu - \nu_e)$. If these are real heads and are actually of isotopic origin they must all be attributed to the latter molecule.

Again, since the less abundant molecule is heavier than the more abundant, the vibrational displacements, $-0{\cdot}0122\ (\nu - \nu_e)$, of its bands are towards the system origins ν_e throughout. And since the bands of all three systems degrade towards the far ultra-violet, the bands on the low-ν side of the system origins are not favourable to the observation of the isotopic heads, as these lie within the stronger band-structure limited by the neighbouring main heads; such bands form much the greater part of each of the SiCl systems. However, seven of Datta's twelve isotopic heads occur on this side of ν_e in the λ 2942 system. The bands where the isotopic heads are more favourably placed for observation outside the neighbouring strong band-structure are those on the high-ν side of ν_e. Of these, which, unfortunately, are very few in the SiCl systems, the 0,0 band of each system has a very small displacement, $-0{\cdot}0122\ (\nu - \nu_e)$, and the same is true of the 1,1 band (which, moreover, is badly overrun by the 0,0 band) in the λ 2436 system; the 2,0 and 3,0 bands of the λ 2942 system are, as already stated, probably not detected; and the 1,0 band of the λ 2232 system is doubtful and very weak. The only favourable bands are therefore the 1,0 in the λ 2942 system and the 1,0 and 2,0 bands in the λ 2436 system, and it is for just these three bands, and no others, that faint and somewhat doubtful heads measured in the present plates may be assigned to $^{28}Si^{37}Cl$. Being overrun by partially resolved structure of other bands they are not easy to measure, and no great accuracy is claimed for the results, which are given in table 4.

Table 4. Cl isotope effect; observed band-heads of $^{28}Si^{37}Cl$

System	Band-head	Datta			Author			$\nu' - \nu$ calculated
		λ'	ν'	$\nu' - \nu$	λ'	ν'	$\nu' - \nu$	
λ 2942	1, 0 P_1*	2883·72	34667·3	−8·5	—	—	—	−9·5
	1, 0 P_2	2866·64	34873·8	−9·0	2866·53	34875·2	−8·9	−9·5
λ 2436	1, 0 P_1				2397·20	41702·6	−8·2	−9·0
	1, 0 P_2				2386·05	41897·5	−8·2	−9·0
λ 2436	2, 0 P_1				2360·06	42359·0	−17·1	−17·1
	2, 0 P_2				—	—	—	

* Datta uses the Q_1 head which gives $-16{\cdot}3$ cm.$^{-1}$ as the observed $\nu' - \nu$. Datta's other three isotopic heads on this side of ν_e in this system are assigned to his 2,0 and 3,0 bands, which are discussed on p. 571.

§ 5. ACKNOWLEDGMENTS

The writer has pleasure in thanking the Fereday Electors of St John's College, Oxford, for the opportunity they have afforded him of carrying out further spectroscopic investigations; the Rector of the Imperial College, Prof. G. P. Thomson and Prof. H. Dingle for the excellent facilities placed at his disposal in the Astrophysics laboratories of the College; and the Government Grant Committee of the Royal Society for grants for apparatus, some of which has been used in the work recorded in this paper.

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TRANSMISSION OF LIGHT THROUGH A PILE OF PARALLEL PLATES

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ABSTRACT. The transmission of light through a pile of transparent plates is calculated by a simple method which gives incidentally the fractions of transmitted and reflected light passing at any surface in the system.

It is assumed that all the light incident upon each surface is either reflected or refracted regularly, and that the plates and the separating medium are transparent. Previous treatments of this simple case, for instance that of Baker[1], have summed the infinite series of intensities into which the light is split up. The method given below avoids this summation, and at the same time gives a simple formula for the fractions of light passing in either direction at any surface in the system. These latter results have been applied by the writer in an investigation of the photoelectric properties of transparent films, and it was in order to derive them that the method was developed.

It should be noticed first that in the region between two reflecting surfaces the rays considered together make up two beams going in opposite directions, and if we write down the reflection and transmission relations for each of these beams, then automatically we take into account the whole infinite assembly of multiply reflected rays. This underlying idea has already been used by Smith[2] in a more general treatment including scattering and absorption. Secondly, in order to discover how these beams change as we travel through successive regions between surfaces, it is simplest to consider first the end of the system farthest from the incident light, for here everything can be worked out in terms of the beam leaving the system. It is impossible to begin at the other end because, besides the incident light, there is also the unknown amount of reflected light.

n Beginning at the farthest end, let the surfaces be numbered 1 to n. Let the intensity of the light falling on the nth surface in the same direction as the light q_n, p_n incident on the system be denoted by q_n, and that in the opposite direction by p_n. The same letters can be used for both surfaces of a plate because the reflective and transmissive factors are the same for light incident in either direction on a surface. r If r is the reflection factor, the equations for the beams between two surfaces are then

$$p_{n+1} = (1-r)\,p_n + r q_n \qquad \ldots\ldots(1),$$

$$q_n = (1-r)\,q_{n+1} + r p_{n+1} \qquad \ldots\ldots(2).$$

Adding equations (1) and (2) we get

$$q_{n+1}-p_{n+1}=q_n-p_n.$$

Therefore $$q_{n+1}-p_{n+1}=q_n-p_n=\ \ldots\ =q_1-p_1=q_1,$$

since $$p_1=0.$$

Substituting for q_n in equation (1) we have

$$p_{n+1}=p_n+rq_1.$$

Therefore $$p_{n+1}=p_1+nrq_1=nrq_1,$$

and $$q_{n+1}=(1+nr)\,q_1.$$

The actual value of q_1 for a given set of plates will be proportional to the amount of light falling on the system; and as we are only concerned with the ratios of the beams, q_1 may be taken as unity. Thus

$$p_{n+1}=nr \qquad \ldots\ldots(3),$$

$$q_{n+1}=1+nr \qquad \ldots\ldots(4).$$

For a system with n surfaces, the incident light q_n must be taken as $1+(n-1)\,r$. The transmitted light will be $(1-r)\,q_1$, i.e. $(1-r)$. The fraction transmitted by a system of N plates ($2N$ surfaces) is therefore

$$\frac{1-r}{1+(2N-1)\,r},$$

and the fractions passing at any place in the system are obtained from equations (3) and (4).

The general effect of reflection on photometric measurements has also been treated by Smith in a later paper[3] in which the above expression for the transmission is derived as a special case.

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WOOD-WATER RELATIONSHIPS, 2: THE FIBRE SATURATION POINT OF BEECH WOOD

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ABSTRACT. In order to determine the fibre saturation point of beech wood as accurately as possible, the vapour-pressure isothermal at high relative vapour pressures is measured on small blocks at 23° C., both for the adsorption cycle and for desorptions from three moisture-contents of 83, 47 and 120 per cent, the last value representing approximately complete saturation of the cell structure. Whereas on adsorption a vapour pressure indistinguishable from saturation appears to be reached at about 45 per cent moisture-content, which is much higher than that indicated by most routine methods, it is shown that on desorption the vapour pressure drops slightly at a moisture-content of about 90 per cent and also that the shape of the subsequent desorption curve is considerably influenced by the initial saturation moisture-content from which the drying commences. The observation made by Urquhart[13] on natural cotton, that the first desorption cycle is not reproducible once the material has been completely dried, is found to apply also in the case of beech wood. It is pointed out that there is no discontinuity in size between the botanical and colloidal capillaries and that therefore the fibre saturation point cannot be defined, except as an approximate point at which the change of moisture-content begins to produce an appreciable effect on the particular property of wood under consideration.

§ 1. INTRODUCTION

OWING to the practical importance of knowing the amount of water which wood will take up in a saturated atmosphere, a special term, the *fibre saturation point*, has come to be used for this value. It was originally defined by Tiemann[1] as the moisture-content at which further reduction causes an increase in strength of the wood, but it is now more generally described as the moisture-content at which the cell wall is saturated with water but the cell cavities empty[2] or as a value analogous to the limit of absorption of liquid by a jelly[3] which means in effect that it is the minimum moisture-content in equilibrium with a saturated atmosphere; the word "minimum" being required because wood may retain in the cell spaces large quantities of free water.

For purposes of routine measurement in this and other Forest Products Laboratories, the fibre saturation point is estimated from the moisture-content at which certain discontinuities occur in the change of the physical properties of the wood with moisture-content[2,4]. The properties usually investigated are: the maximum crushing strength parallel to the grain and the shrinkages in the radial and tangential directions. The fibre saturation point has also been determined by Stamm[3] from the change in electrical conductivity of wood.

Table I gives the average results obtained in this laboratory on a large number of specimens for six separate consignments of Beech and those quoted by Stamm for Sitka spruce.

The wide discrepancy between these values for the fibre saturation point has thrown doubt on the validity of such methods, but whatever the limitations of these indirect methods, the true fibre saturation point may be defined provisionally as the dividing line between the free and bound water in the wood, and moisture may be said to be "bound" when it exerts a vapour pressure less than saturation. The present experiments were undertaken to try to determine the true fibre saturation point in this way.

The {vapour pressure, moisture-content} isothermal (in future referred to as "*the isothermal*") has been determined for a few woods[5,6,7,8] and these show a curve similar in shape to those found for other hygroscopic materials, such as cotton[9]. They also show the usual hysteresis; that this hysteresis is of practical importance in the equilibrium moisture-content of wood in normal use has been shown by Knight in this Laboratory[10]. Since in practice the isothermal curves are drawn through a series of experimental points it is not unusual to take the

Table 1. Comparison of fibre saturation points by routine methods

Laboratory consignment number	Specific gravity*	Fibre saturation point by			
		Maximum crushing strength (per cent)	Shrinkage		Electrical conductivity
			Radial (per cent)	Tangential (per cent)	
Beech (F.P.R.L.)					
10	·562	24·9	27·1	34·1	—
23	·541	23·8	27·5	35·3	—
24	·548	23·9	26·5	34·7	—
35	·561	24·3	27·2	34·2	—
40	·580	24·0	24·3	34·0	—
46	·548	25·4	25·4	31·0	—
Sitka spruce (F.P.R.L.) 25	·356	25·0	23·6	26·1	—
(Stamm)	—	27·0	28·0	30·0	29

saturation point reached on adsorption as the starting point for the desorption curve also[7] giving thus a loop which closes at the saturation value. It was noticed, however, that if, after saturation had apparently been reached, the first desorption points were taken for very small reductions in moisture-content a disproportionately large drop in the vapour pressure occurred. This phenomenon was observed on cotton by Urquhart and Williams[9] and by Lavine and Gauger[8] for wood and lignite.

The shape of the desorption curves suggests that a lowering of the vapour pressure would be found at moisture-contents considerably higher than the adsorption saturation value, implying that the hysteresis, so far from vanishing at the saturated vapour pressure, might be considerably greater at saturation than at any other vapour pressure. On the other hand, if measurements could be made with infinite accuracy it is possible that the true saturation moisture-content on adsorption would also be found to be much higher than had generally been supposed.

* I.e. dry weight/green volume.

§ 2. APPARATUS AND METHOD

A method was, therefore, evolved by which artificially high moisture-contents could be reached by free distillation of water on to the wood. Extreme accuracy in the measurement of the moisture-content had to be sacrificed but at high vapour pressures, where the changes in moisture-content are large, this limitation is relatively unimportant. The quartz spring method of McBain and Bakr[11] is not suitable for the present work because (1) artificially high moisture-contents had to be obtained and it would be impossible to prevent an unpredictable extra extension of the spring due to condensation on the spring itself. (2) The smallest impurity of the water supply would slightly lower the maximum vapour pressure obtainable so that true saturation might never be attained and (3) at saturation the slightest variation in temperature would cause free distillation on to or off the wood and no definite end-point would be found. It was, therefore, decided in seeking the saturation moisture-content to start from moisture-contents below the expected value and, by distilling small quantities of water on to the wood, to rise to others greatly in excess of it; the resulting equilibrium vapour pressure at each step being compared with the maximum obtainable by distilling some of the water into the connecting tubes of the apparatus. The saturation value was to be taken as the point of junction of the isothermal with the saturated vapour pressure line.

It has been usefully stressed by Pidgeon[12] that the maximum width of the hysteresis loop will not be attained if adsorption takes place always from a saturated vapour pressure. This source of error is small, however, and in these experiments, where all readings are practically at saturation, it is likely to be negligible. In any case, such evidence of hysteresis as is found will be the more convincing since, on Pidgeon's argument, the method here used should lend a slight bias towards its elimination.

The apparatus shown diagrammatically in figure 1 was therefore constructed, consisting of two bottles A (only one shown) containing the wood, a bottle B containing water, a tap T_1 leading to a manometer M, another tap T_2 leading to the P_2O_5 drying tube and thence through a flexible tube to the hyvac pump. The tap T_3 served to admit air slowly through a leak L, while the bulb V (200 cm.^{3}) gave additional volume to the manometer space. This glass work was supported on a frame which could be lowered into a water bath at $23{\cdot}00 \pm 0{\cdot}02°$ C. The bottles A were of about 10 cm.^{3} capacity and fitted with a cap so made that a quarter turn closed the hole H when the bottles were removed at the joint J for weighing. The bottle B was similar except that it also contained a small coil of nickel-chrome wire which, when electrically heated, caused slow evaporation of the water. To keep the tops of the bottles A dry, a diving bell D with a lead ring R as sinker was used as shown, resting on part of the frame; the bottoms of A being in the water of the bath so as to be efficiently controlled in temperature. B was completely covered by D. To open and close the bottles while in the bath, glass rods, which extended horizontally beyond the edge of D, were joined to the bottles and to the tap T_1, so that these could be turned from above with a glass hook. This was

important because if the bottles were open while being lowered into or removed from the bath, considerable migration of moisture could take place owing to temperature differences inside *D*.

The manometer *M* was of 18-mm. bore, the limbs being connected by a length of 2-mm. tubing to prevent a rush of mercury when air was admitted. The heights were read through the plate-glass side of the tank to 0·05 mm. or by judgment to 0·02 mm. on a Casella cathetometer which gave a magnified image of the meniscus. Each reading taken near saturation was compared with the saturation value obtained by closing *A* and opening *B* without otherwise altering the setting, and checked

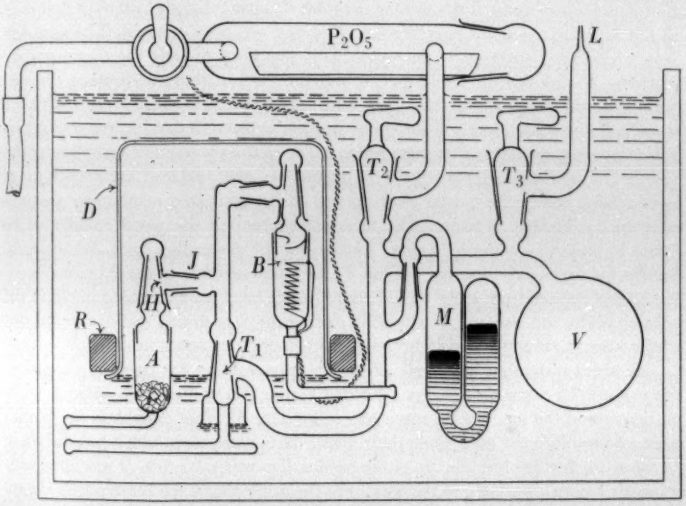

Figure 1. Diagrammatic sketch of apparatus.

against the reading obtained after a misty condensation had been obtained in the connecting tubes of the apparatus by warming *B*. A correction was also made for slight variations in temperature at the time a reading was taken. Under these experimental conditions it was considered that relative vapour pressures of 0·1 per cent or less could be detected, and of 0·25 per cent measured with reasonable accuracy.

The bulb *V* was useful in reducing pressure errors due to slight air leaks (which occasionally occurred because the bottles had to be removed for each weighing) but chiefly because, in the event of a leak, the bottles could be evacuated without loss of moisture by repetitions of a cycle involving, firstly the evacuation of the space between T_2 and *H*, then the saturation of this space with water vapour and

finally opening *H*. This method was also used for the initial evacuation of the samples and of the water in *B*.

§ 3. PROCEDURE

Approximately 0·5 g. of air-dry beech, cut into about 2-mm. cubes to ensure that all the cells were cut open at least once, was placed in each bottle *A*. These were evacuated without drying, and left all day* to reach equilibrium with the manometer. If no heat was supplied to *B*, the wood usually took up from about 35 to 40 per cent of moisture which is higher than the values given in table 1, but on being isolated from *B* the vapour pressure dropped slightly, showing that even at this moisture content the saturation value had not been reached. The next step was to condense water on to the wood. This was done outside the thermostat by warming *B*, and slightly cooling *A*, round the bottom only, with ether. In this way moisture condensed on the glass wall only where it was in contact with the wood and was subsequently absorbed by it, leaving the wall dry. It was shown that this temporary cooling had no measurable effect on the subsequent behaviour of the wood. The bottles being closed, the apparatus was now replaced in the bath for at least 1 hour before the bottles were opened to the saturated manometer space to take up equilibrium pressure. The moisture-content of the wood could thus be raised by steps to any desired value. Finally, for the desorption cycle, drying could be effected by slightly opening the tap T_2 for a few seconds to the P_2O_5 in *D*.

As will be seen from table 2 a few slight desorptions were included in the initial wetting cycle, and also one readsorption during the first drying cycle. Subsequent cycles were made continuously between the wet and dry conditions.

To avoid unwanted hysteresis effects on reassembling for further adsorption, the manometer space was always saturated before the bottles were opened, while on desorption the manometer space had to be dry. If, after weighing, the bottles were lowered into the bath while their upper parts were surrounded by cool air in *D*, moisture distilled into the cap of the bottles. To overcome this, *D* was filled with warm air before lowering into the tank. For the same reason the bottles were always handled by the cap during weighing.

Tests made on the empty bottles to determine whether condensation on the glass walls was appreciable, showed that errors from this cause could easily be avoided. The dry weight of the wood, on which all moisture-contents are based, was taken at the end of each drying cycle, by evacuating strongly over P_2O_5.

§ 4. RESULTS

The results are shown in table 2 where the desorption values are printed in italics, while figure 2 gives those for bottle 2 only. The adsorption saturation value is certainly higher than any of the values recorded in table 1, but the increased

* In general the bottles were left to set up equilibrium with the manometer for some 20 hours. A few tests were made by leaving them from 2 to 4 days but these were indistinguishable on the curve, so it may be assumed that equilibrium is established in 20 hours.

accuracy of measurement has had the paradoxical result of making the true saturation point more difficult, rather than easier, to determine because the more closely saturation is approached the more nearly does the isothermal curve lie parallel to the saturation line. Indeed, if these points are plotted to the nearest 0·5 per cent relative vapour pressure the effect of a decrease in accuracy is clearly seen because the saturation value would be judged to lie at a much lower moisture-content.

First cycle. Whereas the adsorption saturation appears to be reached at about a moisture-content of 45 per cent, the first desorption point tends to fall below saturation at a moisture-content of about 78 per cent and the line is consistently below for all subsequent readings. Thus within the degree of accuracy claimed, there appears to be a hysteresis amounting to a moisture-content of some 30 per cent at saturation. It should, however, be noted that on the first adsorption curve there is a tendency for the vapour pressure to lie on the low side of saturation up to a moisture-content of about 60 per cent, although the assumed limit of accuracy makes it possible that these points should in fact coincide with the saturation line. It might, therefore, be held that the adsorption and desorption fibre saturation points are identical and that the hysteresis loop closes at some very high moisture-content. This observation of delayed saturation is not, however, supported in the second wetting cycle where a pressure indistinguishable from saturation is reached at a moisture-content of 46 per cent. Only by extreme precision could this point be settled experimentally.

There is further evidence in these results to show when saturation is approached on adsorption. When the samples in the two bottles are adsorbing, they will do so initially at slightly different rates which will depend on chance causes, but while equilibrium is being set up they will come ultimately to the same moisture-content (except for possible slight differences due to hysteresis effects during the moisture exchange). Close to saturation, however, there will be practically no vapour pressure gradient and the moisture-contents will in general remain different. This is well shown in the last column of table 2 where for example reading No. 40 shows equal moisture-contents of 40·6 per cent, whereas for No. 41 the moisture-contents are different. On desorption, however, we are in general starting from different moisture-contents and when the vapour pressure begins to drop the tendency for the moisture-contents again to equalize will be masked because each sample will tend to follow its own isothermal and, as these may be very different in the initial stages, equalization of moisture-content will be delayed till quite low vapour pressures have been reached; see readings 17 to 23, 41 to 46 and 57 to 68.

Second and third cycles. The difference between the moisture-contents of the two samples on desorption emphasized the possible influence of the initial moisture-content on the position of the desorption curve while another possible factor is the effect of complete desiccation on the subsequent hygroscopicity, such as was noticed by Urquhart[13] on cotton taken direct from the boll which showed higher moisture-content values in this state than after the first drying cycle had been completed. The beech used here was similar to the natural cotton because it had been neither

Table 2*

No.	Relative vapour pressure (per cent)	Moisture-content (per cent)		Differences between bottles	No.	Relative vapour pressure (per cent)	Moisture-content (per cent)		Differences between bottles
		Bottle 1	Bottle 2				Bottle 1	Bottle 2	
4	100·5 (leak)	36·4	36·0	+ 0·4	36	56·0	10·0	9·4	+0·6
5	*98·8*	*34·6*	*33·7*	+ *0·9*	37	78·6	16·0	15·5	+0·5
6	99·8	36·6	36·0	+ 0·6	38	98·9	31·9	31·5	+0·4
7	99·8	36·7	35·9	+ 0·8	39	99·8	36·0	35·7	+0·3
8	Slight accidental desorption. Not measured				40	99·9	40·6	40·6	0·0
9	99·8	43·3	45·3	− 2·0	41	100·0	46·6	47·2	−1·1
10	*99·3*	*41·4*	*42·2*	− *0·8*	42	*99·8*	*43·7*	*44·3*	−0·6
11	—	48·9	53·8	− 4·9†	43	*99·6*	*41·1*	*41·1*	*0·0*
12	—	*44·3*	*51·4*	− *7·1*	44	*99·3*	*38·5*	*38·7*	−0·2
13	99·9	54·0	59·4	− 5·4	45	*99·0*	*36·0*	*36·1*	−0·1
14	*99·8*	*51·8*	*55·8*	− *4·0*†	46	*98·0*	*33·7*	*33·4*	+0·3
16	100·0	71·6	83·1	−11·5	47	*95·6*	*31·0*	*30·8*	+0·2
17	*99·8*	*68·3*	*78·0*	− *9·7*	48	*93·7*	*29·1*	*28·9*	+0·2†
18	*99·7*	*64·9*	*73·6*	− *8·7*		Dry weight taken here			
19	*99·7*	*61·4*	*69·0*	− *8·6*	53	100·0	120·2	121·8	−1·6
20	*99·5*	*58·4*	*65·1*	− *6·7*	54	*100·0*	*118·8*	*120·5*	−1·7
21	*99·7*	*54·7*	*59·8*	− *5·1*	57‡	*100·0*	*98·4*	*107·4*	−9·0
22	*99·6*	*51·6*	*54·3*	− *2·7*	62‡	*99·9*	*81·4*	*90·1*	−8·7
23	*99·5*	*46·6*	*46·7*	+ *0·1*	63	*99·8*	*75·9*	*84·5*	−8·6
24	*98·9*	*44·7*	*44·5*	+ *0·2*	64	*99·7*	*67·7*	*74·7*	−7·0
25	*98·5*	*43·0*	*42·3*	+ *0·7*	65	*99·6*	*57·8*	*63·3*	−5·5
26	*97·3*	*40·6*	*39·9*	+ *0·7*†	68	*99·1*	*42·7*	*43·7*	−1·0†
27	*93·9*	*35·5*	*35·0*	+ *0·5*	69	*98·5*	*40·4*	*41·0*	−0·6
28	*93·4*	*32·4* ?	*33·4*	− *1·0* ?	70	*95·8*	*35·2*	*35·2*	*0·0*
29	*92·3*	*33·0*	*32·6*	+ *0·4*	71	*92·7*	*30·2*	*30·9*	−0·7
30	99·5	41·4	41·0	+ 0·4	72	*89·5*	*25·1*	*25·9*	−0·8
31	99·6	41·7	41·3	+ 0·4	73	*63·2*	*13·2*	*12·9*	+0·3
32	*99·3*	*40·1*	*39·7*	+ *0·4*	74	*18·7*	*5·2*	*5·3*	−0·1
33	*96·5*	*38·3*	*38·0*	+ *0·3*		Final dry weight taken here			
34	*41·9*	*8·6*	*8·6*	*0* †					
	Dry weight taken here								

* Desorption values are printed in italics.

† Bottles regreased at these points.

‡ The missing entries here refer to desorptions which showed no drop in vapour pressure. The weights were therefore not taken.

completely dried nor resaturated since felling. If, therefore, Urquhart's observation is applicable also to wood, the effect of the initial moisture-content should be sought only after the first drying cycle is completed.

A second drying cycle was therefore taken (nos. 41 to 48) from 47 per cent and a third (nos. 53 to 72) from 120 per cent moisture-content, which represents approximately complete saturation of the botanical structure. Comparison of cycles 2 and 3 indicate that the effect of initial moisture-content is at first appreciable, but that the two curves converge as the vapour pressure is lowered; while the reduced hygroscopicity after drying is clearly shown by the fact that the moisture-contents of the third cycle are lower than those of the first although the initial moisture-

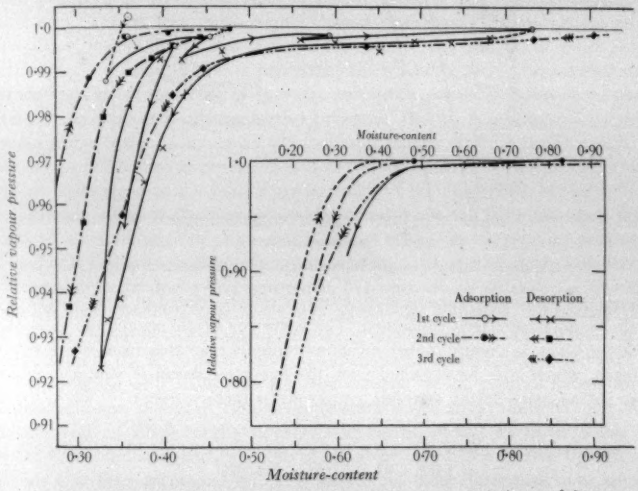

Figure 2. Vapour-pressure isothermal of small beech-wood blocks at 23° C.

content is somewhat higher. The check weighings of the dry wood taken at the end of each cycle agreed sufficiently well to show that these results are not due to experimental error, and it will be noticed by comparing the moisture-contents of the two samples at lower vapour pressures that this error does not exceed 1 per cent. The inset of figure 2 gives the outside envelopes of the three cycles in order to stress these observations.

Sitka spruce. Some measurements were also made on Sitka spruce flour at 23° C. These were done before it was fully realized that the initial moisture-content from which drying was commenced would alter the position of the desorption curve. The highest moisture-content reached was only 65 per cent, so the desorption curve shown in figure 3 must not be taken as representative of the maximum hysteresis obtainable. The values are less accurate than those for beech because the

use of flour instead of blocks added considerably to the experimental difficulties. None the less the general accuracy of the lower part of the curve (0–90 per cent relative vapour pressure) has been established by comparing it with the very accurate determination by Filby and Maass[6] at 20° C. on White spruce, which,

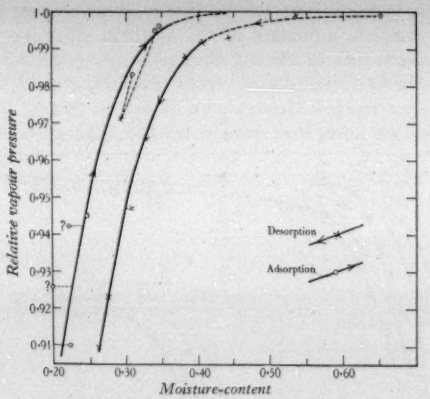

Figure 3. Vapour-pressure isothermal of Sitka spruce flour at 23° C.

though not identical in botanical structure, is closely related to Sitka spruce as far as the wood substance is concerned. The curve for White spruce lies throughout its lower range at slightly higher moisture-contents than that from which figure 3 is taken, which is to be expected from the lower temperature, and also perhaps from the intensive drying methods, employed by these workers.

§ 5. CALCULATION OF THE FIBRE SATURATION POINT FROM THE CELL-SPACE RATIO

If we adhere to the definition of the fibre saturation point as the moisture-content at which the cell spaces are empty but the cell walls are full, we can calculate the fibre saturation point, provided we know d, the specific gravity* of the wood block, ρ that of the wood substance and A the cell space ratio[14] of the block when saturated with water.

In 1 cm.³ of block there will be d/ρ cm.³ of wood substance and $(1-d/\rho)$ cm.³ of water and if m is the fibre saturation point there will be md cm.³ of water held in the cells and A cm.³ in the spaces, hence

$$md=\left(1-\frac{d}{\rho}\right)-A,$$

$d=0{\cdot}54$ may be taken as a representative value for beech and the cell-space ratio of a microsection of this specific gravity, as determined by the Wood Structure Section

* I.e. dry weight/green volume.

of this Laboratory, is approximately 0·42. Assuming that the adsorbed water retains its normal density, as is required for this calculation, ρ may be taken as very close to 1·54[15]. This gives the fibre saturation point as about 43 per cent.

§ 6. DISCUSSION

As was stated in the first paper of this series[16] it is generally agreed that, near the saturation value, at least some of the water is held by surface tension in the fine capillaries of the cell wall and that the effective radii of these capillaries may be calculated from the desorption isothermal. Now the desorption curve, figure 2, shows a drop to 99·9 per cent relative vapour pressure at a moisture-content of 90 per cent. This is very much higher than the calculated fibre saturation point given above, and indicates that it is the moisture in the cell spaces which is responsible for this drop. Fibres of beech may easily be detected whose internal radii near the ends are of the order of 10^{-4} cm. and which would, therefore, hold water at roughly 99·9 per cent relative vapour pressure. Due to local irregularities some portions of the botanical structure will have still smaller effective capillary radii so that the effect of botanical capillaries will be observable in the present experiments and may well extend to the vapour pressure of 98·6 per cent which corresponds to the calculated value of the fibre saturation point. Thus the fibre saturation point should be of significance in producing a sudden change in the physical properties of wood only if there is a discontinuity in capillary sizes at that point. This should be observable in the desorption isothermal, but since clearly no such discontinuity exists we must conclude that there is a continuous gradation of capillary sizes between the botanical and colloidal structures. The same conclusion is reached by consideration of the absorption curve which shows no definite saturation value.

The influence of a change in moisture-content on the physical properties of the wood will not, therefore, become apparent at any discrete value but only very gradually and, as all physical properties will not be equally sensitive to this influence, the wide discrepancies in the fibre saturation point indicated by different methods is at once accounted for. The reasons for these differences have already been briefly discussed[17] and will form the subject of further communications. It may also be noted that fundamental physical properties of wood, such as the heat of wetting[7] or the adsorption compression[18], also gradually approach limiting values as the moisture-content is raised and do not indicate definite saturation values.

Thus the fibre saturation point given in § 5, which cannot be calculated accurately, is of little significance from the point of view of its physical effects.

§ 7. CONCLUSION

These experiments were originally undertaken to test the validity of routine methods of determining the fibre saturation point of wood. It is obviously impossible to use exact measurements of the vapour pressure isothermal as a routine method on hundreds of individual samples of numerous species. Instead, the

methods mentioned at the beginning of the paper, are generally adopted [2,4] since the required data form part of the practical information, which it is the purpose of routine testing to supply.

Since the conclusion has here been reached that the term "fibre saturation" refers to a range of moisture-contents rather than to a discrete value, it may seem that the values of the fibre saturation point given in table 1 are of doubtful utility, but it should be borne in mind that from the point of view of working conditions each does represent the point at which a change in moisture-content begins to produce an appreciable effect on the particular property under consideration and is of great importance, provided that it is only used in relation to that property.

§ 8. ACKNOWLEDGMENTS

In conclusion I should like to thank the Director of the Laboratory, Mr W. A. Robertson for permission to publish this paper, and the Wood Structure Section for their cooperation in the measurement of the cell-space ratio.

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DISCUSSION

Dr D. T. Davies. I have discussed this paper with Mr Barkas previously and I make this contribution largely at his request because somewhat similar work is being carried out on coal and there are certain points of interesting similarity and divergence. In the screening, dedusting and dry-cleaning of coal, freedom of movement of separate particles is essential, and many processes fail entirely if surface moisture is present.

The terms "inherent" and "surface moisture" are very loosely used in the coal industry. The former should, of course, be defined at a definite relative humidity, and account should be taken of the hysteresis effect which exists in coal as in other materials of gel structure. The figures quoted for inherent moisture probably approximate to the values that would be obtained in equilibrium at a relative humidity between 50 and 60 per cent, and they vary from about 1 to 10 per cent according to the nature of the coal. Manufacturers of dry-cleaning plant usually expect to encounter difficulties if more than 2 per cent of moisture in excess of the inherent moisture is present in the coal, but it is hardly possible that such a fixed figure should really apply to all coals.

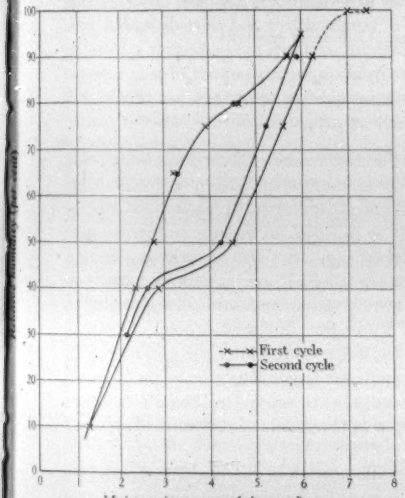

Figure 1. Isothermal of Meltonfield coal at 25° C.

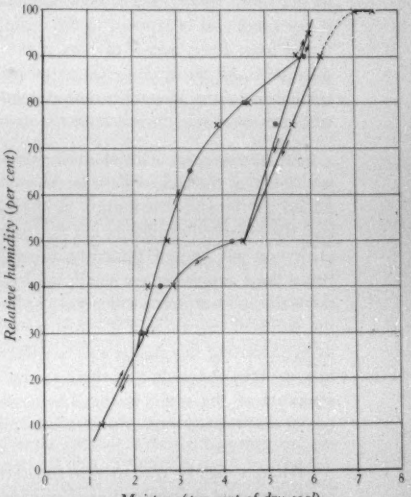

Figure 2. Isothermal of Meltonfield coal at 25° C.

A study of the mechanics of moisture-retention is being made by the Fuel Research Organization, and figure 1 shows a typical vapour-pressure isothermal produced by Dr Slater of the South Yorkshire Survey Laboratory by drawing a smooth curve through the equilibrium points. The irreversible part of the isothermal on the extreme right of the diagram was obtained by taking sample drillings from a shot-hole bored in the actual coal face below ground. It will be noted that the moisture-content of the freshly mined coal was nearly 7·5 per cent whereas in equilibrium at a relative humidity of 95 per cent the moisture-content is only 6 per cent.

In figure 2 I have taken the liberty of drawing a slightly different curve through the same points with a view to stressing the possibility of a correspondence between

the isothermals for coal and silica gel. The most important part of the curve for our purposes is the range over relative humidities of about 90 per cent, and although the data regarding this range are not nearly so complete as those put forward for wood by Mr Barkas, I have made certain observations regarding them which may be of interest.

The hysteresis loop appears to be definitely closed at a relative humidity of about 90 per cent and the range above that appears to be reversible and to correspond to true surface moisture. The point at which freedom of relative movement of particles occurs in a mass of drying coal has been termed the "dusty point" and occurs at the moisture-content corresponding to a relative humidity of about 95 per cent. In addition to these laboratory experiments it has been observed that if dry small coal is exposed to the ordinary temperatures and humidities but protected from direct access of rain, it can pick up so much moisture that it loses its dustiness. All the evidence thus appears to indicate the appearance of true external surface moisture in equilibrium at relative humidities below 100 per cent and in sufficient quantities to influence the mechanical properties of the coal.

Author's reply. The observations of Dr Davies are of interest in supporting my view that the shape of the isothermal for wood near saturation is largely determined by the size-distribution of the botanical capillaries. I understand that in coal the botanical capillaries are not empty as in wood, so that the isothermal near saturation will be determined by the colloidal capillaries and by surface sorption. Since these capillaries are small, the hysteresis effect, if due to delayed wetting of the wall on adsorption, will persist only up to a vapour pressure corresponding to the radius of curvature of the meniscus in the largest capillaries present. Owing to delayed wetting this radius will be somewhat larger than that of the capillary itself, but one may conclude that there are no capillaries larger than this in the colloidal structure of the coal. If the Thomson equation is valid, Dr Davies's figure of 90 per cent relative vapour pressure corresponds to a radius of curvature of approximately 10^{-6} cm.

While it may be true that, in the reversible portion of the isothermal, sorption on the external surface will predominate, it must be remembered that the concave menisci mentioned above will also sorb moisture at relative vapour pressures above 90 per cent until at saturation the menisci will be plane. Thus the total sorption of 6 per cent moisture-content at saturation will be the sum of the surface and capillary sorptions. The capillary sorption between a relative vapour pressure of 90 per cent and saturation will be reversible, for within this range the meniscus is always in contact with the lip of the capillary and there is no effect of delayed wetting.

621.383.2

TIME LAG IN PHOTOELECTRIC CELLS

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AND

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ABSTRACT. § 1. This work continues that of Campbell and Stoodley[1] and of Campbell[2]. § 2. Frequency-response curves are compared with oscillograph traces of the current through the cell when light is suddenly thrown on or off it. A theory of the comparison is given; it is shown that the comparison provides a test of the "assumption of independence", i.e. the assumption that time lag arises wholly in processes following a single instantaneous light-impulse, and not from the interaction of succeeding impulses. The experiments are wholly adverse to the assumption; low-frequency time lag must arise in great part from such interaction. The evidence on which the assumption was based previously is re-examined; it is found to be exceptional and not typical, and therefore quite inconclusive. § 3. Attempts to determine directly how time lag is affected by the size of the cells, other things being as far as possible equal, failed because it was evident that factors other than those contemplated were being varied accidentally. But measurements on a single long cell with several anodes indicated that low-frequency time lag is not due directly to the finite velocity of the ions. Incidentally the positive ion current was found—as is to be expected—to show greater time lag than the whole current. § 4. The experiments on cells cooled in liquid air, described in paper II, were continued; the previous results were confirmed; temperature has an effect separate from that on the density of the gas. § 5. The very small time lag of argon-filled cells with sensitized potassium cathodes was found to be due to hydrogen evolved from the cathode. When this is removed the time lag increases greatly. Further investigation of this remarkable result is deferred. § 6. In a brief discussion it is pointed out that the distinction previously made between low-frequency and high-frequency time lag must be maintained; the latter is undoubtedly due to the finite velocity of the ions, the former is not. For the low-frequency lag metastable states are still the most plausible explanation; but there are difficulties in the failure of the assumption of independence and in the effect of hydrogen. No alternative theory is proposed at present; more facts are required.

§ 1. INTRODUCTION

THIS paper describes a continuation of the work of Campbell and Stoodley[1], and of Campbell[2]. These two papers will be referred to as *paper I* and *paper II* respectively. The new work will be described first with reference to these two papers only; its relation to the work of others will be discussed later.

* Mr Stoodley is a past, not a present member of the Staff.

§ 2. GENERAL THEORY

Calculation. The theory underlying much of paper II may be stated thus. If
L_0 light of intensity L_0 falls on the cathode only for an infinitesimal period $d\tau$ at time
τ, q $\tau = 0$, then the charge q that has crossed the cell up to time τ is given by
k
$$q = kL_0\, d\tau . f(\tau) \qquad \text{.....(1)},$$
$f(\tau)$ where $f(\tau)$ increases very rapidly at $\tau = 0$, and is equal to 1 for all values of τ greater
T than some limit T, which may be identified with the time lag.

So far the theory is hardly dubitable. But if it is to be of any service in explaining the effects of time lag, and in particular the form of the frequency-response curve, a further assumption must be made. It is that the effects of successive light-impulses are independent, and that if the light L incident on the cell is varying continuously, so that

$$L = L_0\, \phi\,(t) \qquad \text{.....(2)},$$

then the charge that has passed up to any given moment (from which the current can be obtained by differentiation) can be calculated by adding the effects, given by equation (1), of all the infinitesimal impulses into which the continuously varying light can be resolved. This assumption appears to have been made by most of those who have attempted to relate the form of the frequency-response curve to the physical processes that are assumed to give rise to the time lag. Nevertheless it is by no means necessarily true; it may well be that the ions produced by earlier impulses affect materially (e.g. by the development of space charges), the number of ions produced by later impulses and the time that they take to reach the electrodes.

In paper II an attempt was made to decide the matter by direct determination of $f(\tau)$ in equation (1) and the comparison of the frequency-response curves calculated from $f(\tau)$ so determined, by the aid of the assumption of independence, with experimental frequency response curves. But the direct determination is very difficult. The first part of the work described here aimed at an indirect determination of $f(\tau)$. The indirect determination involves the assumption of independence; nevertheless it appeared that the method, though it could not establish the truth of the assumption certainly, might produce conclusive evidence of its falsity, if it is indeed false.

The theory of the method is as follows: Suppose there is thrown on the cell light varying according to the thin line in figure 1; light is thrown on the cell suddenly at $t = 0$, maintained constant for a time T so long that $f(T) = 1$, cut off suddenly, kept off for time T and so on. Then, as is known from paper I, the current
i i through the cell will vary according to the thick line. (Of course the ordinates for the thin and thick lines are different; the maximum in each case is made equal to 1.) Then, if the assumption of independence is true, it can be proved that the equation of the part of the thick line, starting from $t = 0$, is

$$i/kL_0 = f(t) \qquad \text{.....(3)},$$

t_1 and the equation starting from $t = T$, putting $t_1 = t - T$ is

$$i/kL_0 = 1 - f(t_1) = (\text{say})\, f_1(t) \qquad \text{.....(3')}.$$

The ascending and descending curves should be superposable, and each should give $f(\tau)$ directly.

Before equations (3) and (3′) are proved, it should be noted that it is impossible to turn the light on and off with perfect suddenness; the light will really vary as shown by the dotted line, taking a time θ to rise and fall. It is therefore well to take this complication into account from the start.

Equations (3) and (4) of paper II, on which calculations were based previously, are incorrect; accordingly the theory will be set forth entirely anew.*

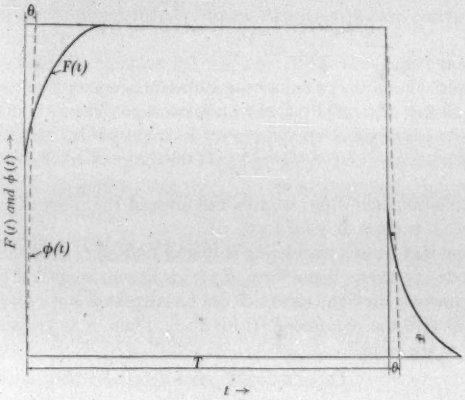

Figure 1.

If L is given by equation (2), the charge given to the electrode by a light impulse, lasting a time $d\tau$ and occurring at an interval τ before the instant of observing t, is, in virtue of equation (1),

$$q = kL_0\,\phi\,(t-\tau)\,f(\tau)\,d\tau \qquad \text{.....(4).}$$

The whole charge Q that has been communicated since the start of the experiment at time t_0 is, in virtue of the assumption of independence, given by

$$Q = kL_0 \int_0^{t-t_0} \phi\,(t-\tau)\,f(\tau)\,d\tau \qquad \text{.....(5).}$$

The current at time t is given by

$$i = dQ/dt \qquad \text{.....(6).}$$

Consequently

$$i/kL_0 = \frac{d}{dt}\int_0^{t-t_0} \phi\,(t-\tau)\,f(\tau)\,d\tau \qquad \text{.....(7).}$$

The experiment assumes that T is so long that the *current* at t is not affected by events before $t-T$. Hence in equation (7), but not in equation (5), we can change

* More conventional, and perhaps more stringent, proofs can be based on the accepted formulae of electric circuit theory. We prefer to start from the ultimate facts in this example.

the upper limit of integration to T; the limits are then independent of t and the differentiation can be performed within the integral. Hence

$$i/kL_0 = \int_0^T \phi'(t-\tau) f(\tau)\, d\tau \qquad \text{.....(8),}$$

θ $\phi'(t-\tau)$ is zero, except when $t-\tau$ lies between 0 and θ. If we confine our attention to values of $t > \theta$, $\phi(t-\tau)$ changes from 0 to 1, while τ changes from $t-\theta$ to t. In the limit when $\theta = 0$, $f(\tau)$ is constant and equal to $f(t)$ during this change. So that

$$i/kL_0 = f(t) \int_{t-\theta}^{t} \phi'(t-\tau)\, d\tau = f(t) \qquad \text{.....(9).}$$

This is equation (3).

If θ is appreciable, we may assume with sufficient accuracy that the rise and fall of ϕ is linear, so that $\phi'(t-\theta) = 1/\theta$ when it is not zero. Then

$$i/kL_0 = \frac{1}{\theta} \int_{t-\theta}^{t} f(\tau)\, d\tau \qquad \text{.....(10).}$$

$F(t)$ We shall call this function $F(t)$; it gives the form of the thick curve in figure 1 when θ is finite; it is given only for $t > \theta$.

The problem that we are considering is that of finding $f(\tau)$ when $F(t)$ is given from the cathode-ray trace. If the form of $f(\tau)$ is known analytically, but not the value of its parameters, the right-hand side can be integrated and a set of parameters sought that will give the required $F(t)$ for $t > \theta$. Thus, it is known that $f(\tau)$ is approximately of the form

a, λ $$f(\tau) = 1 - ae^{-\lambda\tau} \quad (\tau > 0) \qquad \text{.....(11).}$$

a' This gives $$F(t) = 1 - a'e^{-\lambda t} \qquad \text{.....(12),}$$

where $$a' = a\frac{e^{\lambda\theta} - 1}{\lambda\theta} \sim a\left(1 + \frac{\lambda\theta}{2}\right) \qquad \text{.....(13).}$$

$F(t)$ then differs from $f(t)$ only in the substitution of a' for a. If we find λ and a' from the given $F(t)$, a can be found from equation (13) if θ is known, and thus $f(t)$ determined. The frequency response curve can then be calculated and compared with the experimental curve.

If the form of $f(\tau)$ is not known and $F(t)$ is given graphically, but not analytically, $f(\tau)$ in equation (10) can be expanded by Taylor's theorem, leading to

$$F(t) = f(t-\theta) + \frac{\theta}{2} f'(t-\theta) + \ldots, \quad t > \theta \qquad \text{.....(14),}$$

which can be solved for $f(t)$ by graphical approximation. It should be observed that, in this process, we obtain only $f(\tau)$ for $\tau > \theta$; since there may be a discontinuity at $\tau = 0$, extrapolation to zero is precarious. But any reasonable extrapolation will lead to the same frequency response curves from frequencies much less than $1/\theta$.

All this applies only if $\theta < t < T$. The corresponding treatment when $T + \theta < t < 2T$ is so similar that it need not be given. It follows quite generally

that, so long as the fall of $\phi(t)$ at $t=T$ is similar to the rise at $t=0$ and occupies the same time θ, then, if F_1 corresponds to F as f_1 to f in equation (3′) F_1, f_1

$$F_1(t_1)=1-F(t) \qquad \text{.....(15).}$$

The rise and fall of the thick line in figure 1 should be superposable.

It remains to consider how the frequency response curve is to be calculated from $f(\tau)$ derived in this way. This curve is a relation between $i_a/\bar{\imath}$ and n, the n frequency of the light varied sinusoidally, so that equation (2) becomes

$$L=L_0(1+e^{j\omega t}), \quad \omega=2\pi n \qquad \text{.....(16),} \quad \omega$$

where i_a is the amplitude of the alternating component of the current through the i_a cell, $\bar{\imath}$ the main current. $\bar{\imath}$

We start again from equation (7), and now divide the range 0 to $t-t_0$ into two ranges: (1) 0 to m/n, where m is an integer so great that $f(m/n)=1$ (that is to say, m, n a large number m of complete periods extending backwards from t) and (2) m/n to $t-t_0$. For range (1) the limits of integration are independent of t, and we can differentiate within the integral; for range (2) $f(\tau)=1$. Consequently

$$i/kL_0=\left|\frac{d}{dt}\int_{m/n}^{t-t_0}(1+e^{j\omega(t-\tau)})\,d\tau+\int_0^{m/n}j\omega\,.e^{j\omega(t-\tau)}f(\tau)\,d\tau\right| \qquad \text{.....(17).}$$

Remembering that $e^{-j\omega m/n}=1$, we have

$$i/kL_0=\left|1+e^{j\omega t}+e^{j\omega t}.j\omega\int_0^{m/n}e^{-j\omega\tau}f(\tau)\,d\tau\right| \qquad \text{.....(18),}$$

$$\bar{\imath}/kL_0=1; \quad i_a/kL_0=\left|1+j\omega\int_0^{m/n}e^{-j\omega\tau}f(\tau)\,d\tau\right| \qquad \text{.....(19).}$$

Hence, trigonometrical functions being introduced,

$$i_a/\bar{\imath}=\{(1+A)^2+B^2\}^{\frac{1}{2}} \qquad \text{.....(20),}$$

where

$$\left.\begin{aligned}A&=\omega\int_0^{2\pi m/\omega}\sin\omega t\,f(\tau)\,d\tau\\ B&=\omega\int_0^{2\pi m/\omega}\cos\omega t\,f(\tau)\,d\tau\end{aligned}\right\} \qquad \text{.....(21).} \qquad \begin{matrix}A\\ B\end{matrix}$$

A and B can be determined by graphical integration, when $f(\tau)$ is given graphically; since $f(\tau)$ increases with τ, both A and B are always negative.

In the special case* when $f(\tau)$ has the form (11),

$$i_a/\bar{\imath}=\left\{\frac{1+(1-a)^2y^2}{1+y^2}\right\}^{\frac{1}{2}}, \quad y=\omega/\lambda \qquad \text{.....(22).}$$

Experiments. Frequency-response curves were taken as described in paper II. It is to be noted that the variation of the light was not strictly sinusoidal; but a very superficial inquiry suffices to show that the results described below are not affected by this slight departure from ideal conditions. The input resistance to the first valve of the amplifier was also so small that the capacity of the cell might be

* Equation (7) of paper II is identical with equation (22), if a misprint is corrected, and $a\omega^2\lambda^2$ replaced by $a^2\omega^2\lambda^2$. Accordingly, though equations (3) and (4) of paper II are incorrect, they lead to the right result.

taken as zero. The slight variation of amplification with frequency was ascertained by measuring the response of a vacuum cell without time lag and allowed for.

The cathode-ray oscillograph was of standard design and requires no special description. Here again a small input resistance was used. The interruption of the light, giving $\phi(t)$ the form of the dotted curve in figure 1, was effected by a rotating disc, whose edge was recessed over half its circumference. The boundary between the recessed and non-recessed half was radial; the width of the beam interrupted was such that $\theta = 1/20{,}000$ sec. The disc was rotated at 50 revolutions per second by a synchronous motor so that (in figure 1) $T = 1/100$ sec. The supply to the motor provided the time-base. The image on the screen was traced on tracing paper; it was enlarged and transferred to squared paper by optical projection.

The time $t = 0$ could always be identified by a sharp corner in the trace, but the location of the exact point was one of the main sources of error. Another source was an inclination of the flat part of the trace to the horizontal, due doubtless to the usual change of the sensitivity of the cell when current is drawn from it. The possible error arising in these and other ways is indicated in the figures below by the breadth of the curves.

The cells examined were almost all cathode-on-the wall cells, the cathode being Ag-O-Cs; the filling was usually argon, but sometimes helium. The shapes and the pressure of the argon were various; though these features affected the form of the frequency-response curves greatly, they did not seem to affect in any simple manner the relation between this curve and the cathode-ray trace. Accordingly details need not always be given. Measurements were usually made at several values of the gas factor m and the mean current $\bar{\imath}$; of course, the time lag always increased with m and, to a lesser degree, with $\bar{\imath}$. Most of the facts detailed below refer to $m = 10$ and $\bar{\imath}$ = about 2 μA.; but again precise details in every case are unnecessary.

Results. There was a general qualitative correlation of the kind to be expected, between time lag indicated by the frequency-response curve and time lag indicated by the cathode-ray trace; that is to say, the more rapidly $i_a/\bar{\imath}$ decreased with increase of frequency, the more slowly did $F(t)$ approach 1. If m or $\bar{\imath}$ were varied in a single cell, the correlation appeared to be perfect. But in the comparison of different cells, apparent departures from correlation were obvious at once; very similar cathode-ray traces sometimes corresponded to very different frequency-response curves, especially when the gas filling was different.

Further it was found that the rise and the fall of the cathode-ray trace were not superposable, as they should be according to equation (14); the difference was sometimes small; sometimes the rise was steeper, sometimes the fall. Examples of a small and a large difference of opposite signs are given in figures 2 and 3; here the curve marked Rise is $F(t)$ for $\theta < t < T$; the curve marked Fall is $F_1(t_1)$ for $\theta < t_1 < T$.

The first of these observations suggested, the second proved, that the theory expressed in equations (1) to (22) is not accurately true; for similarity of rise and fall is an inevitable consequence of the assumption of independence. Nevertheless an attempt was made to apply the results of that theory quantitatively. For this

purpose the following procedure was adopted. Examples were selected in which $F(t)$ approached the form (12) and $i_a/\bar{i}$ approached the form (22). A family of

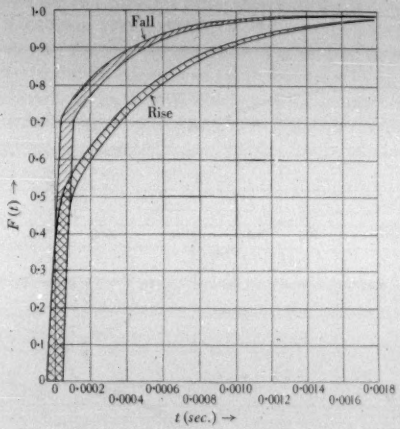

Figure 2. Rise and fall curves for small spherical cell argon filling: $m = 10$.

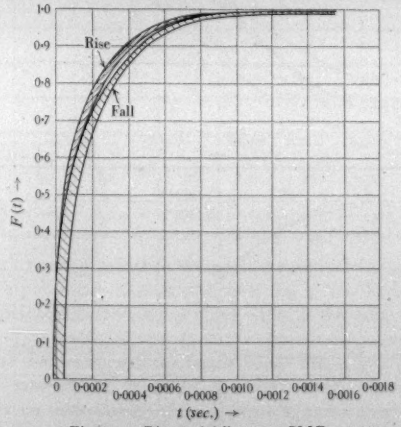

Figure 3. Rise and fall curves CMG 1.

curves $z = 1 - a'e^{-\lambda t}$ for various values of a' were plotted with $\log \lambda t$ as base; the full curves in figures 4, 6 and 8 are members of this family, the scale of abscissae being that at the top. $F(t)$, taken from the mean of the rise and fall curves, was now plotted against $\log t$. This curve was placed over the family, with the lines $z = 1$ z

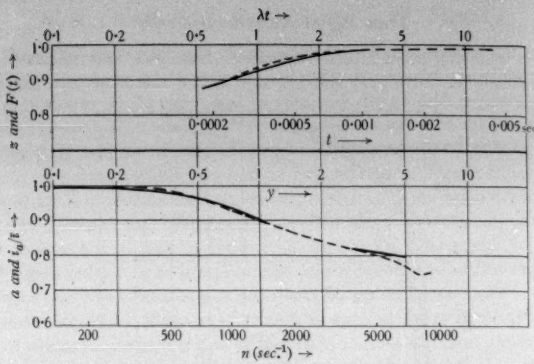

Figure 4. z against λt and $F(t)$ against t when $a'=0{\cdot}2$, $a=0{\cdot}18_8$, $\lambda=3250$.

Figure 5. a against y and i_a/I against n when $a=0{\cdot}2$, $\lambda=8490$.

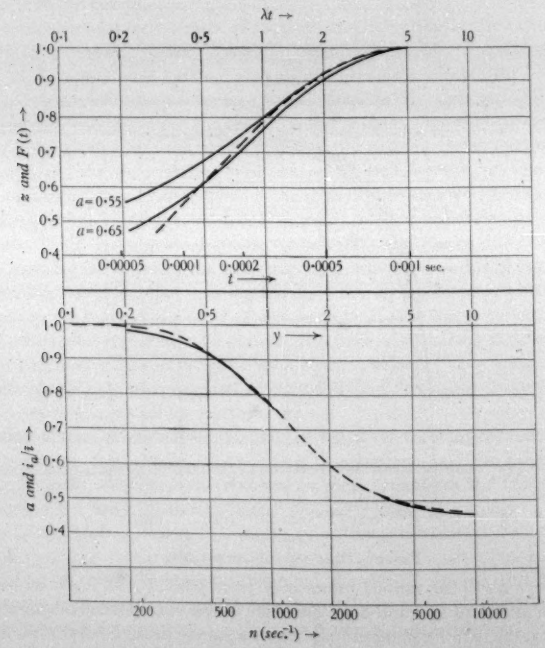

Figure 6. z against λt and $F(t)$ against t when $a'=0{\cdot}6$, $\lambda=3970$, $a=0{\cdot}55$.

Figure 7. a against y and i_a/I against n when $a=0{\cdot}55$, $\lambda=5500$.

and $F(t)=1$ coincident, and moved parallel to this line until the best fit between $F(t)$ and one of the family was obtained; the result is indicated by the dotted curve (where distinct from the full curve), t being shown on the lower scale. If t' is now the value on the lower scale corresponding to $\lambda t=1$ on the upper scale, the appropriate value of λ is $1/t'$; the appropriate value of a' is that for the member of the family with which the dotted curve most nearly coincides. The values of a' and λ thus deduced are shown on the figures, together with a deduced from equation (13).

A similar procedure was adopted for $i_a/\bar{\imath}$. A family of curves (22) for different values of a were plotted against log y; members of this family are given by the full

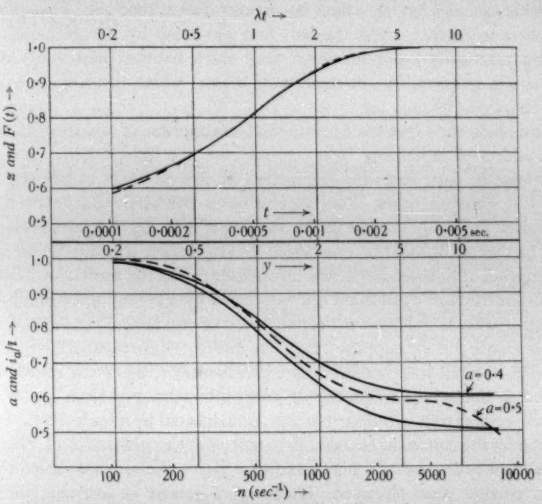

Figure 8. z against λt and $F(t)$ against t when $a'=0{\cdot}5$, $\lambda=1940$, $a=0{\cdot}47_8$.
Figure 9. a against y and $i_a/\bar{\imath}$ against n when $a=0{\cdot}42$, $\lambda=3270$.

lines in figures 5, 7 and 9, which correspond respectively to figures 4, 6 and 8. The frequency-response curve, plotted against log n, was brought into the best coincidence, as indicated by the dotted curve. If n' is the value on the lower scale corresponding to $y=1$ on the upper, then the appropriate value of λ is $2\pi n'$; a is given as before by the member of the family which fits.

We have thus two pairs of values (a, λ) which should coincide if the theory is true. It will be seen that, though there is some agreement in the as, λ deduced from $i_a/\bar{\imath}$ is always much greater than λ deduced from $F(t)$. The discrepancy is far beyond any experimental error; graphical integration, based on equations (14) and (20), showed that it could not be explained by the fact that $f(\tau)$ is not accurately of the form (10). The experiments prove definitely that the theory of equations (1) to (22) does not apply, and hence that the only dubitable assumption, namely that of independence, is not true.

It may be observed that this conclusion is supported even by the agreement found, namely that between the as $1-a$ is a measure of the fraction of the current that is substantially free from time lag; the agreement of the as indicates that this fraction can be deduced approximately both from $F(t)$ and $i_0/\bar{\imath}$. If $(1-a)$ turned out to be the fraction carried by the primary current, namely $1/m$, the explanation would be obvious; but actually $(1-a)$ is always much greater than $1/m$; for $m=10$ in all these examples. It appears then that there is a part of the current carried by ions or secondary electrons, and not by the primary electrons, which has no time lag, or at least a time lag less than 1/10,000 sec. (see § 6 below) and another part carried by the same agencies having a time lag greater than 1/1000 sec. The only explanation appears to be that, while the ions first produced by the primaries reach the electrodes practically instantaneously, they leave behind them some effect (e.g. space charges, polarizations, or metastable atoms) which cause the ions produced later to be subject to time lag.

We conclude then that the fundamental assumption of our theory is false, and that the effects of succeeding light impulses are not independent; time lag must arise, at least in part, from the interaction of the products of primary electrons produced at different times. This conclusion is not surprising in itself, and has been involved implicitly in some of the theories of time lag that have been proposed. But one further point must be examined. In paper II it was urged that a denial of the assumption of independence was inconsistent with the ascertained fact that the mean current through a gas-filled cell, produced by a given light beam interrupted by a rotating disc, is independent of the speed of rotation.

The evidence for the supposed fact was therefore re-examined. The mean current through the cell was measured by a galvanometer, while the speed of the disc was varied so that n, the frequency of interruption, ranged from 200 to 8000 per second; the greater part of the current was compensated by a second cell. Sensitivity was limited by the continual change of current under a constant light, characteristic of all gas-filled cells used at a high gas factor; nevertheless undoubted changes of the mean current were observed. They varied greatly in amount; the previous failures to detect changes were due to the unfortunate selection of a cell in which they were particularly small, and to the use of small mean currents.

$\bar{\imath}_1$ Table 1 gives some results. In the fifth column $\bar{\imath}_1$ is the mean current at $n=8000$
$\bar{\imath}_2$ and $\bar{\imath}_2$ the mean current at $n=200$.

It is to be observed that $\bar{\imath}_1/\bar{\imath}_2$ is always less than 1 and decreases as either $\bar{\imath}$ or m is increased; there is no close correlation between $\bar{\imath}_1/\bar{\imath}_2$ and the time lag, but in any particular cell they increase together, as is to be expected. Some further observations on this matter are recorded in the next section. The value of $\bar{\imath}$ in the frequency-response curves of figures 5, 7 and 9 is that appropriate to $n=8000$; but in these curves the variation of $\bar{\imath}$ is negligibly small.

The only evidence for the theory that has been discussed is destroyed. With it goes a favourable approach to the problem of determining the physical processes underlying time lag; for if $f(\tau)$ existed and could be determined, it would be relatively easy to test various suggestions concerning these processes. This possi-

bility has to be abandoned. The rest of the paper deals with some miscellaneous experiments made in the hope of finding a clue to some other approach.

Table 1

Cell	Gas factor m	Mean current (μA.)	Time lag $\bar{i}_2/\bar{i}$ ($n=8000$)	$(1-\bar{i}_1/\bar{i}_2)\times 100$
CMG 7 (large cylindrical)	10	4	·71	0·7
	10	2	·73	0·4
	5	2	·81	0·2
CMG 22 (small cylindrical)	9	6	·71	6·0
	9	1·2	·76	2·5
	4	7	·85	2·0
	4	2	·87	1·5
CMG 24 (spherical)	10	7	·52	7·0
	10	4	·54	4·0
	5	4	·77	1·7

§ 3. THE EFFECT OF THE SIZE OF THE CELL

The question how the time lag varies with the size of the cell is not determinate. For how are other relevant factors to be varied with the size, e.g. the gas pressure, the applied voltage and the current? It appeared that conditions might be comparable if the cells were all spherical, contained the same mass of gas, were operated at the same m, and at a current so small that time lag is independent of current. A series of spherical cells with cathode on the wall were made up, satisfying these conditions. But from the irregularity of the results it was concluded that some other factor must be varying, probably the nature of the cathode and possibly

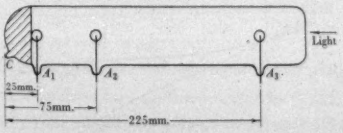

Figure 10.

impurities in the gas (see below); nothing could be concluded except that at the same gas factor the larger cell by no means always had the larger time lag.

In a second attempt a cell of the form shown in figure 10 was constructed and filled with argon. It will be seen that there are three small anodes A_1, A_2, A_3 at 25, 75, 225 mm. from the hemispherical cathode C covering one end of the cell. Many experiments were made with this cell; but only two need be recorded.

In one experiment two frequency-response curves were compared: (1) with A_1 as anode and A_2, A_3 connected to the cathode; (2) with A_3 as anode and A_1, A_2 connected to the cathode. The gas factor was the same ($m=10$) in both cases; the voltages applied to the anode to attain this gas factor were 111 V. in (1) and 206 V. in (2). Since the distance of A_3 from the cathode is 9 times that of A_1, the mean velocities of the electrons and ions must surely have been smaller in (2).

But figure 11, which gives the two frequency-response curves, shows that there was little difference in time lag; certainly at frequencies below 10,000, there is no evidence that time lag depends directly on the speed of any particle along the direction of the field. On the other hand it may depend on a speed of diffusion (e.g. of metastable atoms) perpendicular to the field; for the tube is of uniform bore.

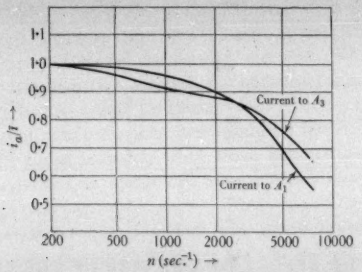

Figure 11. 4-electrode tubular cell, $m=10$, $i=2$ μA.

It may be added that the static characteristic and the frequency-response curve in the long cell were influenced greatly by shields surrounding it; as might be expected, charges on the walls affect the characteristic and through it the frequency response. On the other hand the spherical cells proved once more that these charges cannot be the main cause of low-frequency lag; for these cells had very small windows and very little bare glass, and yet some showed very marked lag.

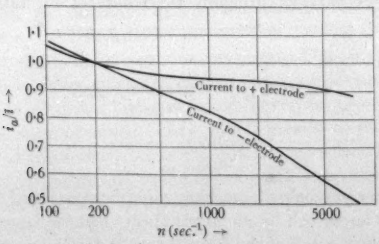

Figure 12. 4-electrode tubular cell.

In the second experiment, A_3 was the anode at 160 V., while A_1 and A_2 were maintained at -60 V. relative to the cathode; A_1 and A_2 then receive only positive ions; the current to A_1+A_2 was about 1/3 of that to A_3. The gas factor of the anode current was 4. The frequency response curves of the current arriving at A_3 and of the current arriving at A_1+A_2 are shown in figure 12; the time lag of the latter current is much the greater. This is, of course, to be expected; for positive ions must always be secondary and produced after the primary electrons; but it is well to be sure that the expected happens. No quantitative conclusions seem possible.

It is to be observed that the value of i_a/i is shown increasing above 1 at low

frequencies. This is because the mean current $\bar{\imath}$ rises rapidly at low frequencies; $\bar{\imath}$ is taken as the value at about $n = 1000$; it is actually greater than this value below $n = 200$, and $i_a/\bar{\imath}$ is not really greater than 1.

§ 4. TIME LAG AND TEMPERATURE

One of the facts recorded in paper II is the variation of the low-frequency time lag with the temperature of the cell. Since this variation was discovered only just before the previous experiments had to be interrupted, some more observations were made to confirm its reality; they were successful.

Although the total amount of gas in a sealed cell, and its average density, are unchanged when the cell is cooled, the distribution of the gas may be altered, for example by condensation on the cooled wall which carries the cathode. Accordingly it was important to discover how far the changes in time lag could be due to such changes. For this purpose a gas-filled cell was attached by a narrow tube to a bulb of approximately equal volume; frequency response curves were taken with (1) cell hot, bulb hot; (2) cell hot, bulb cold; (3) cell cold, bulb hot; (4) cell cold, bulb cold. ("Hot" means at room temperature, "cold" at liquid-air temperature.) The density of the gas in the cell, if there is no appreciable condensation on the

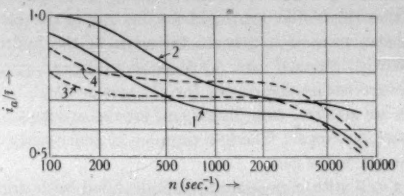

Figure 13. Variation of frequency response with temperature CMG 7 cell, argon filled, $m = 10$.

walls, should be the same in (1) and (4), but greater in (3) and less in (2). Condensation on the cathode-wall should be greater in (3) and (4) than in (1) and (2). The gas factor was adjusted to be the same in all cases; this involved change of the applied voltage.

The results are shown in figure 13, which gives the frequency-response curve for each of the conditions (1), (2), (3) or (4); the applied voltages being 83, 94, 72 and 76. The results indicate that at high frequencies the time lag is determined almost entirely by the density of the free gas in the cell; for at $n > 5000$, curves (1) and (4) are almost the same. But, as was found previously, the low-frequency time lag, indicated by the rate at which the curve falls initially, is greater when the cell is cold. This may be due to a change in the nature of the cathode due to condensation of the argon in it; this explanation, though possible, was not suggested in paper II. On the other hand it may be due to a change in some diffusion process in the gas, as suggested in paper II. These experiments do not enable a distinction to be made, but they confirm very clearly the distinction, made in paper II, between low-frequency and high-frequency time lag; it is clear that one can vary greatly without any great change on the other.

§ 5. EFFECT OF HYDROGEN ON THE TIME LAG

It has long been recognized that cells of the Elster-Geitel type, with cathodes of sensitized potassium, show very much less time lag than modern cells with cathodes of the type Ag-O-M, especially when M is caesium. Since the same gas, argon, is used for filling cells of both types, it has been naturally concluded that the greater time lag of the modern cell is connected with its cathode.

But among the facts recorded in paper I are some observations on *un*sensitized potassium cells; it seemed that these had a time lag much greater than that of the sensitized cells and comparable with that of Ag-O-M cells. But, since the geometrical form of the cells compared was not always the same, the result was not regarded as conclusive.

The matter has been re-examined and the previous result confirmed. Even if the cells are geometrically similar and filled with the same gas at the same pressure, the unsensitized cell shows a marked low-frequency time lag, while the sensitized cell shows none; and even at high frequencies the frequency-response curve is steeper in the unsensitized cell. If this difference were due to the cathode it would be very difficult to explain, for in every apparently relevant property the sensitized cathode resembles the Ag-O-M cathode more nearly than the unsensitized. However it appeared that this difference might not be due to the cathode. Sensitized cells always contain a trace of hydrogen; for some of the hydrogen absorbed in sensitization is slowly liberated later until an equilibrium pressure is reached. Ag-O-M cells never contain hydrogen, for the gas is fatal to their sensitivity. Unsensitized cells are also free from hydrogen, for the unsensitized metal absorbs, rather than liberates, hydrogen. The low time lag of sensitized cells might be due to a trace of hydrogen in the gas.

Accordingly, a cell with a potassium cathode filled with argon was provided with a palladium tube through which hydrogen could be introduced and removed. The series of frequency-response curves shown in figure 14 was obtained; the scale of n is plain, but logarithmic. All were taken at the same m (which means different voltages) and about the same i; ϕ is the primary emission from the cathode in $\mu A/L$ for light at 2800° K.

Originally the potassium was unsensitized and no hydrogen was present; there is large low-frequency lag and low emission (*a*). When a little hydrogen was added, the lag decreased greatly; the emission was also greatly decreased (*b*). After 18 hours the emission had increased again, but the lag had decreased further and indeed almost vanished (*c*); but after 72 hours, much of it had reappeared (*d*). The changes (*c*) and (*d*) may be attributed to absorption of the hydrogen by the cathode, which however retained the metallic appearance of the unsensitized metal.

A considerable quantity of hydrogen was now introduced and a discharge was passed, so that the cathode acquired the colour characteristic of the sensitized metal and the emission increased. The hydrogen was removed; the time lag was considerable (*e*); after 48 hours, during which hydrogen was probably evolved, the time lag was less (*f*); by adjusting the quantity of hydrogen by trial, a curve approaching (*b*) could be obtained.

These and similar experiments prove conclusively that the presence of hydrogen in relatively small quantities affects the time lag profoundly. The difference between (*a*) and the remaining curves suggests that part of the difference may lie in gas absorbed on the cathode; for if hydrogen was absorbed between (*a*) and (*b*) it would not be removed by subsequent events. The next step is clearly to deter-

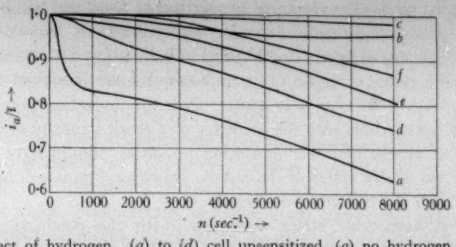

Figure 14. Effect of hydrogen. (*a*) to (*d*) cell unsensitized. (*a*) no hydrogen, $\phi=0{\cdot}33$; (*b*) on addition of hydrogen, $\phi=0{\cdot}05$; (*c*) 18 hours after addition of hydrogen, $\phi=0{\cdot}03$; (*d*) 72 hours after addition of hydrogen, $\phi=0{\cdot}42$; (*e*) on sensitization of cell and removal of excess hydrogen, $\phi=0{\cdot}80$; (*f*) 48 hours later, $\phi=0{\cdot}90$.

mine quantitatively the hydrogen present at the various stages; but the determination is attended by some experimental difficulties which had not been surmounted when the work had to be interrupted. Further examination is therefore deferred. But it may be observed that, except when the cathode was being sensitized—for instance between (*d*) and (*e*)—the amount of hydrogen present was always too small to affect the colour of the discharge; the argon must always have been ionized, and there was much evidence that the time lag was a minimum for some optimum amount of hydrogen, and greater for either greater or less amounts.

§ 6. DISCUSSION OF RESULTS

All the frequency-response curves in these experiments were taken at frequencies less than 10,000. They all confirm the view that the low-frequency time lag, operative at these frequencies, is distinct from the high-frequency lag operative at 20,000 c./sec. and upwards. Further, Roggendorf[3] has shown that at sufficiently high frequencies time lag eliminates all but the primary photoelectric current, so that $i_a/\bar{i}=1/m$. As was pointed out above, there is no sign in these experiments of an approach to this limit. Again it may be taken as certain that the high-frequency time lag is due partly, if not wholly, to the finite velocity of the ions and to the time that they take to travel between the electrodes[3,4,5]*. It follows that this finite velocity is not responsible for the low-frequency lag.

As an explanation of low-frequency lag, the presence of metastable atoms, suggested by Schroeter and Lubszynski[6], is plausible, as was indicated in § 3. However, there are some difficulties.

* In view of the criticisms of Kvartskhava and Timofeev it may be well to point out that we have never denied that the high-frequency lag is due to this cause; our remarks applied only to the low-frequency lag. Their experiments, in which they assume that there is no time lag below 1000 c./sec. throw no light on this lag.

Schroeter and Lubszynski suggested that the smaller time lag in argon, as compared with neon and helium, might be due to effect of impurities on the metastable states of this gas; the experiments described in § 5 might seem to support this view. But we are not clear that hydrogen should have the effect they suggest. Penning's theory, universally accepted, of the effect of hydrogen in changing the sparking-potential (and other electrical properties) of neon and helium rests on the fact that the ionization potential (16·1 V.) of hydrogen is less than the energy of the metastable states of neon (16·5 V.) and of helium (19·8 V.). But the energies of the metastable states of argon (11·5 and 11·7 V.) are less than the ionization potential of hydrogen, which is also greater than the ionization potential of argon (15·4 V.). It is not obvious why the presence of a small quantity of hydrogen in a large quantity of argon, of lower ionization potential, should have any effect in destroying the metastable states of the latter. However Penning[9] has stated, as a fact, that hydrogen has this effect on argon.

Moreover, if metastable states disappear, with the production of charged carriers, by reaction with the unionized gas or with the walls, any time lag due to metastable states should accord with the assumption of independence; the products of successive light impulses should interact only if the metastable atoms react with charged carriers or with each other. The proof that this assumption is false is not easy to reconcile with any simple theory that attributes time lag to metastable states.

The remaining theories proposed are those of Fourmarier[7] and Kingdon and Thomson[8]; the former associates time lag with ionization by positive ions, the latter with thermal changes produced in the cathode by the impact of positive ions. The former is either a variant of Ollendorf's theory, or requires us to suppose that the individual ionizations by positive ions take time—a supposition for which there is no evidence. The latter theory, not very definite in any case, does not seem easily reconcilable with the experiments described in §§ 4 and 5.

We do not propose to put forward any theory of our own, for though there is evidence that the nature of the cathode, and particularly gas absorbed on it, has some effect, none of the obvious explanations of that effect seem satisfactory. Our object is rather to insist that the facts concerning low-frequency time lag are much more complicated than has been generally recognized; that none of the theories proposed hitherto take account of the complexities, and that many more experiments will be required before any new theory can be tested adequately.

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DISCUSSION

Mr L. TRELOAR. In connexion with the theory that attributes the time-lag to the presence of metastable atoms, one of the authors stated that such atoms, on striking the cathode, were supposed to give rise to the emission of secondary electrons. Is there any evidence to suggest that secondary emission would in fact take place as a result of such a process?

AUTHORS' reply. It is theoretically probable that the energy stored in metastable atoms is available to liberate electrons from the atoms of solid bodies as well as from the atoms of gases, and we believe that there is some experimental evidence for such liberation, but "secondary emission" may not be an appropriate term for it. If, as de Boer holds, photoelectric emission from composite cathodes is photo-ionization of adsorbed atoms, surely the ionization of such atoms by collisions of the second kind is almost inevitable.

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THE RELATION BETWEEN RATE AND ARC FOR A FREE PENDULUM

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ABSTRACT. When a pendulum swings about a centre in a vacuum the well-known circular deviation gives the increase of period with amplitude. For the case in which the pendulum is suspended by a spring the period has been calculated but not the change with amplitude. The presence of air increases the period in three ways: for two of these the amount has not been computed and may depend on amplitude. Thus for the ordinary clock pendulum, apart from the effect of the impulse, experiment is necessary to compare the real amplitude deviation with the computed circular deviation. In about 1856 J. M. Bloxam recorded a change of rate between two amplitudes of only one-half the circular difference. The writer, on the other hand, has found five rates which fit the circular deviation within less than 1 per cent.

§ 1. AMPLITUDE, CIRCULAR AND IMPULSE DEVIATIONS

THE experiment described in §§ 4 to 17 of this paper gives reliable results, for one pendulum at least. Many horologists may be doubtful about observations made with a variable temperature, but other observations proved that, with the pendulum used, the effect of temperature on rate could be accurately allowed for (§ 16). Temperature-control would not have added materially to precision since the weakest link in the experimental chain is the decrement-determination (§ 13). Judgment was needed in drawing the smooth curve from which values were to be read for computing impulse deviations. This judgment was not biased by the general result of the experiment as it was exercised before I realized what this result would be.

By amplitude deviation I mean the loss in seconds per day of a free pendulum, α when swinging through a finite arc 2α radians, which keeps true time when the arc is infinitesimal. A constituent of amplitude deviation is circular deviation* computed on the assumption that the centre of gravity moves in a circle. If the maintaining impulse of a clock imposes an impulse deviation on the pendulum, relative values of amplitude deviation are found by deducting impulse deviation from observed clock rates. "Amplitude"† means the semi-arc α.

Prof. R. A. Sampson, referring to amplitude deviation in *Studies in Clocks and Time keeping*[1], says that he "reserves the question whether this quantity is ade-

* Often called "circular error". It seems preferable to use "error" to mean change of rate due to unit change of α. Then the error is the differential coefficient of the deviation with regard to amplitude.

† Unfortunately, "arc" and "semi-amplitude" also are used for α in clock literature.

quately represented by circular deviation." When the pendulum turns about an ideal knife-edge (see § 18) and swings *in vacuo*, no such reservation is necessary. Rate then changes with arc solely because the centre of gravity moves in a circle so that central acceleration is proportional, not to an angle, but to its sine. The circular deviation is easily computed[2]. For amplitudes up to 2° the circular deviation = 86,400 $\alpha^2/16$ to the nearest millisecond per day.

§ 2. SIMPLE CIRCULAR DEVIATION DOES NOT NECESSARILY APPLY TO A SPRING-SUSPENDED PENDULUM MOVING IN AIR

When the pendulum is suspended by a spring, this adds to the restoring moment due to gravity. Moreover the centre of gravity no longer moves in a circle. Sampson gives the theory for a uniform spring[3], but he rejects powers of angles above the first in solving the equations, so that no light is thrown on amplitude deviation.

The air or other medium in which the pendulum moves increases the period in three ways. (*a*) Buoyancy reduces the effective weight. This does not affect amplitude deviation as the rate-change is independent of α. (*b*) The air is in motion so the effective mass of the pendulum is increased. The consequent increase in period varies with the shape of the pendulum and its surroundings and it is likely to change with amplitude. (*c*) It is often stated that air resistance has a negligible effect on the period and this would be true were it symmetrical about the vertical. The pendulum, however, moves in air which it has already disturbed, so resistance at any angle before the central position is reached is greater than that at an equal angle after that point, and air resistance consequently increases the period. It is, at least, not evident that the increase is the same for all amplitudes.

Thus, for the ordinary clock pendulum experiment is necessary to compare the real amplitude deviation with the computed circular deviation and the result applies strictly only to the pendulum used and the surrounding conditions (enclosure, air-density and temperature) obtaining during the experiment.

§ 3. SHORTT ERRORS COMPARED WITH CIRCULAR DEVIATION. BLOXAM'S EXPERIMENT

Amplitude deviation is of practical as well as theoretical interest. Thus with a gravity impulse the working conditions should secure that, for a small change in the moment, the fall in impulse deviation will balance increase in amplitude deviation. The irregularities in rate of two Shortt Clocks at Greenwich have been compared with the circular errors[4] (SH_{11} during 10 months, 1926–7, SH_3 during 22 months, 1928–9) showing fair agreement for three-quarters of the time. This throws no light on amplitude deviation, since no estimate is made of the effect of the impulse on rate, and indeed the causes of the amplitude-changes were unknown.

Nearly eighty years ago J. M. Bloxam tried the only amplitude deviation experiment of which I have read. He designed a gravity escapement and applied it to a clock (still going in the Science Museum, South Kensington) which G. B.

Airy described in 1856 as "a better clock than I have ever used as far as I remember". This type of escapement was used by E. B. Denison for Big Ben.

Bloxam experimented with this clock in Madeira between 1854 and 1857 and changed the amplitude from 89 to 115 min. in 1855 or 1856. No details of observations seem available. After the increase of amplitude Bloxam added $1\frac{1}{4}$ lb. of mercury to the bob, as compensation proved deficient at the larger amplitude. After Bloxam's death Airy published[5] the bare result that "after deducting the estimated effect of the action of the escapement there was a difference of rate of 1·24 sec./day, about half the difference of the circular errors" [2·42].

§ 4. THE AUTHOR'S EXPERIMENT ON PENDULUM 11

During the last eight years I have been experimenting with a series of pendulums enclosed in sealed cases and impulsed by gravity levers. In 1930 I fitted a contrivance to one of the brackets for changing the impulse in order to repeat this experiment under modern conditions. For this purpose I used Pendulum No. 11 during March to May, 1934. This pendulum, in spite of faults, is very stable and, as the result showed, behaved well during the experiment. The general principle is very simple. This and the results obtained will be described before details about methods of observation and reduction and other matters are given.

Clock rates were found by comparing time with the Greenwich 10-h. rhythmic signal radiated from Rugby. About half an hour earlier, observations were made each morning of amplitude, pressure and temperature in the sealed case. For a period lasting from 4 to 9 days, during which the impulse had the same value, the mean rate was recorded together with the averages of the other observations. For a new period, the impulse was changed and observations commenced on the following morning.

In order to change the impulse air must be admitted to the case and be pumped out again, so that the air-density was not exactly the same for each period. The densities are proportional to the pressures (read on an aneroid barometer) reduced to the standard temperature of 60° F. The reduced values were those recorded.

§ 5. THE OBSERVATIONS

The observations relating to the eight periods which constituted the experiment are recorded in table 1. The rates there given are, however, not the observed ones, which appear in the first column of table 4. In order to avoid detail at this stage the rates given relate to standard working conditions of air-density and temperature, etc. A rate is + when the clock is gaining. Two thermometers are used. Temperature in the table is that given by the lower one with its bulb just above the bob. Stratification is excess of upper thermometer temperature over lower (see § 15).

Periods are numbered in the order in which experiments were made. Amplitudes were increased from about 40 to 70 min. and it should be noted that observations on 29 min. follow immediately after those for 70 min. and that at the finish (periods

6 to 8) the amplitude is back again around the initial value (too much of the time was devoted to this amplitude). In this way secular change in rate is best detected and least harmful.

Table 1. Observations

Period	Duration (days)	Temperature (°F.)	Stratification (°F.)	Barometer (inches)	Rate* (sec./day)	Amplitude (minutes)
1	9	61·0	1·93	21·315	0·068	39·78
2	4	61·0	2·07	·302	0·600	51·18
3	7	61·3	2·01	·360	1·022	61·60
4	6	67·7	1·77	·290	1·331	70·24
5	6	64·8	1·80	·290	−0·723	29·33
6	5	65·8	1·90	·266	−0·080	37·89
7	4	66·2	1·92	·362	0·012	39·21
8	8	68·3	1·96	·256	0·142	41·19

* Reduced to standard conditions. See table 4.

§ 6. ELIMINATION OF IMPULSE DEVIATION

In table 2 periods are arranged in order of amplitude. The impulse adds the seconds per day shown in column 2 to the free pendulum rate, so that this latter is found by subtracting impulse deviation from clock rate leaving a *losing* rate shown in column 3 which is to be compared with circular deviation (column 4).

Table 2. Reductions (seconds per day)

Period	Gaining rates	Losing rates			
	Impulse deviation	Free pendulum	Circular deviation	Residue	
5	0·775	1·498	0·393	1·105	
6	1·699	1·779	0·656	1·123	Weighted mean 1·097 at 39·71 min.
7	1·821	1·809	0·703	1·106	
1	1·876	1·808	0·723	1·085	
8	2·005	1·863	0·775	1·088	
2	2·899	2·299	1·197	1·102	
3	3·846	2·824	1·734	1·090	
4	4·671	3·340	2·255	1·085	

The clock was regulated for zero rate with amplitude about 39 min. Had it been regulated to gain 1 sec./day all the free pendulum rates would have been smaller by 1: we are concerned not with the rates but only with their differences. To find how far spring and air modify the circular deviation, the next step is to deduct this from the free pendulum rate. In view of Bloxam's results here comes the surprise; the result is about 1·1 sec./day in every case. In other words, the rates found by experiment fit the computed circular deviation values.

This is shown in table 3, where the true value of the residue has been taken as 1·102 sec./day, which has been subtracted from all the free pendulum rates.

The table shows that no value of amplitude deviation differs from the corresponding circular deviation by as much as 1 per cent. It is not quite correct to

label these first quantities "amplitude deviation" because this assumes that the corresponding quantity for infinitesimal amplitude would be 0. Just as Bloxam gets one difference from observations on two amplitudes so here I get *four* results from *five* amplitudes, which fit in with circular deviation.

Table 3. Free pendulum (seconds per day)

Amplitude	Amplitude deviation	Circular deviation	Difference
29·33	0·396	0·393	+0·003
39·71	0·716	0·721	−0·005
51·18	1·197	1·197	0
61·60	1·722	1·734	−0·012
70·24	2·238	2·255	−0·017

Amplitude deviation appears to grow slightly less rapidly with amplitude than circular deviation. No importance can, however, be attached to the differences shown in the table since they are possibly due to inexact values of decrement (§ 13)

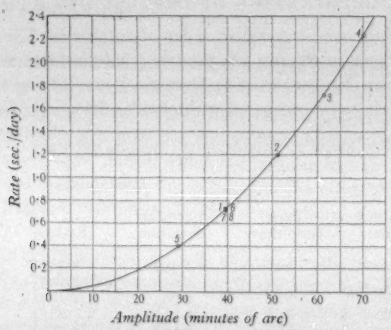

Figure 1. Amplitude deviation. The curve is the *computed* circular deviation. The points are *observed* amplitude deviations.

used in calculating impulse deviation. Changes in δ of less than 0·5 per cent would wipe out all the differences.

The results are shown in figure 1. It must be remembered that the curve is not a smooth curve drawn through the points but a computed curve with which the points derived by experiment are to be compared.

§ 7. RESULT FOR FREE PENDULUM

Thus the resultant contribution to amplitude deviation of the three factors referred to in § 2 is negligible, but it does not follow that the contribution of each is zero. Consequently another pendulum might yield a different result.

Pendulum 11 has a gun-metal bob 7·4 cm. in diameter, 16·0 cm. high, and weighing about 5740 g.; and an invar rod 0·8 cm. in diameter weighing 440 g. The

Elinvar suspension spring is 1·08 cm. long and 1·27 cm. wide. It is mostly 0·0137 cm. thick but is heavier at the top. The pendulum is housed in a cylinder about 20 cm. in diameter. Case and pendulum are carried on brackets bolted into 2½ cwt. of concrete keyed into a 14-in. wall. Energy-dissipation is notably higher when the pendulum is in the case than when in the open. Some details of the experiment will now be given.

§ 8. DETAILS OF EXPERIMENT

"Amplitude" for a pendulum turning about a centre can mean but one thing, but that is not so with a suspension spring. In practice a linear displacement is observed and this is converted into angular measure by dividing by a radius. From what centre shall the radius be measured? One reasonable choice would be the centre of curvature of the path of the centre of gravity. I make another choice by regarding amplitude as the maximum inclination of the rod to its mean position. In this case the centre is the intersection of the moving rod with its rest position, a point for pendulum 11 about 1·4 mm. below the centre of curvature. Accurate measurement of amplitude in this experiment is necessary not only to relate it to the clock rate but also for finding decrement and impulse angles in order to compute impulse deviation. Adequate arrangements are not usually made for this measurement with precision clocks.

§ 9. SCALE-READING BY MICROMETER

I read the scale (which is situated on the top of the bob) by means of a micrometer eyepiece placed above the top plate of the case. For this purpose a plate-glass window is provided in the brass plate and a lens 34 cm. below forms an image of the scale in the focal plane of the eyepiece. The index is a sharp V and is moved by means of a screw whose head is divided into 100 parts, 53 corresponding to a minute of amplitude. A reading is obtained by setting the index first on a scale division at one extremity of the swing and then on another division at the other extremity. The angle between the two scale divisions and the difference between the readings on the micrometer head combine to give the amplitude. For accurate setting it is necessary to observe a scale line several times as it flashes into its stationary position. The amplitude can then be read to 0·01 min., say half a second of arc. When amplitude is changing, as in measuring decrement (§ 13) or angle of impulse (§ 12) or with pendulums which are not impulsed each cycle, determinations must be made rapidly and the results are less precise.

The ivory scale is illuminated by a lamp placed outside the glass cylinder of the case. This scale contracted 0·7 per cent after being placed in the dry air of the case but its dry length has not changed to a readable extent (0·02 per cent) during 4 years. The observed reading is reduced to true minutes by correcting for ruling errors and then deducting 1·1 per cent, corresponding to a distance 92·07 cm. of scale from the turning point.

§ 10. METHOD OF READING WITH BRIGHT LINES

Another kind of scale, which I adopted in 1932 for bracket *F* (which is used for testing half-second pendulums) makes the reading of amplitude more rapid. This is one of Julius Rheinberg's beautiful grainless graticules, a negative with transparent lines on an opaque field. A beam of light, entering the case through the micrometer window, is twice reflected so as to pass through the scale up to the micrometer. To set on a line, the index is moved until its tip is just visible on the background of a bright line in its stationary position. There is no need to judge of coincidence: you either see the tip or you do not. Allowance is made for the fact that the setting is near the edge of the line instead of its centre. This system is better suited for measuring the changing amplitudes referred to above[6].*

§ 11. THE IMPULSE

Motion is maintained by an impulse lever in connexion with an armature arm moved by an electromagnet between a front stop and a back stop[7]. When the impulse lever is not moving with the pendulum it is supported by the armature arm, which is then against its front stop. When the pendulum has swung through an angle θ_1 to the left it picks up the lever and carries it forward up to full amplitude

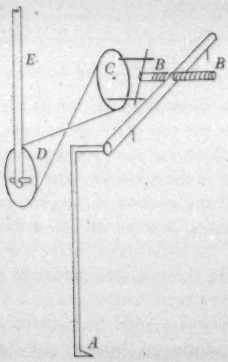

Figure 2. Impulse changer.

and back again. Meanwhile the arm has moved to its back stop, which is adjusted so that the lever is not removed from the pendulum until this has reached angle θ_1 to the right. The extra movement to the right through $2\theta_1$ enables the lever to deliver energy to the pendulum. The arm returns the lever to the initial position ready for a repetition of this cycle of events.

* Mr F. Hope-Jones (*Electric Clocks*, p. 226) says that the semi-arc of the Shortt pendulum falls 6 seconds per half-minute. The fall is really only about one-quarter of this, supposing the data of the preceding paragraph to apply to a 7-kg. pendulum with 54 min. semi-arc.

The magnitude of the impulse can be varied by means of a screwed horizontal arm of the lever. Figure 2 represents the lever which presses on the pendulum at A, B being the horizontal arm. Two coupled pulleys C and D are also shown with a rod E operating D by means of a crank.

To change the impulse, air is admitted to the case and the glass is removed from the micrometer window. The rod is inserted through the window and the pulleys can thus be turned. Pulley C, facing B, has two wires parallel to its axis which engage with a cross wire at the head of B. Thus B is turned and a small reverse motion of the crank clears the lever of the pulley wires. The case is then sealed and the pressure is reduced as nearly as possible to its former value.

§ 12. IMPULSE DEVIATION

The impulse deviation is $86{,}400\,\delta \cot \tau/2\pi f$[8], δ being the decrement (§ 13) of the pendulum while $\sin \tau = \theta_1/\alpha$ and f is the frequency, which is $\frac{1}{2}$ for a seconds pendulum. This omits a small rate common to all amplitudes and another rate due to the inertia of the lever amounting to 0·005 sec./day for an amplitude of 40 min. and to 0·004 for the rest. θ_1 was measured by finding the smallest amplitude at which impulsing takes place. Since the armature does not commence to move instantly on make and break of current the value found for θ_1 (26·35 min.) is more likely to be too large than too small. A better way is to use the telephone signal which is audible for changes far too short to move the arm. A small error in θ is not serious since it affects computed deviations all in the same direction but not, of course, to the same extent.

δ

§ 13. LOGARITHMIC DECREMENT

Elementary theory supposes that a pendulum experiences resistance proportional at all times to its velocity. In accordance with this, amplitude drops from α_0 to α in t seconds where $\alpha/\alpha_0 = e^{-\delta t}$, the logarithmic decrement δ being a constant whose value could be found very exactly by observing the time (about 14,000 sec.) needed for amplitude to fall from 80 to 30 min.

In reality, resistance grows faster with velocity than this theory supposes, and δ is not a constant but increases slowly with α, as appears in figure 3. It is necessary, therefore, to observe smaller intervals (400–1500 sec.) needed for small changes (say $2\frac{1}{2}$ min.) of α. Measurements are made by cutting off the supply of energy to the pendulum and setting the micrometer index symmetrically so that scale lines, one at each end of a swing, pass equal distances beyond the index. These distances decrease until finally the lines coincide with the index, one immediately after the other, at time t_1 when the amplitude is α_1. Similar observations are made when the amplitude has fallen about $2\frac{1}{2}$ min. to α_2 at time t_2, and so on.

The value of δ adopted for α_2 is $(\log_e \alpha_1 - \log_e \alpha_3)/(t_3 - t_1)$. A value for α_3 is similarly obtained from observations of α_2 and α_4. Points on figure 3 represent the corresponding values of δ/π and the smooth line is used to provide values for computing the impulse deviations.

Owing to the difficulty of judging coincidences promptly it is not to be expected that the points will lie neatly on a line but, after making observations which seem satisfactory, one is disappointed to find how far the points spread. I have experienced this disappointment many times. It is a curious fact that the points are not distributed at random—a simple, wavy line can be drawn through, or very close to, all the points. Each wave is completed in 57 min. of the experiment, just as if a second pendulum of nearly equal frequency were attached to the bracket.

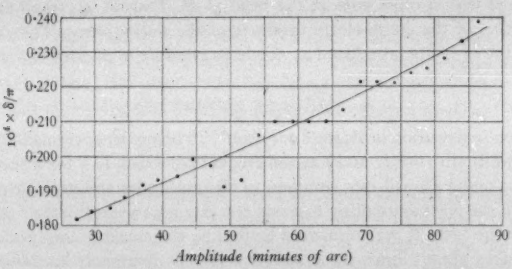

Figure 3. Decrement pendulum no. 11 at 21·3 sec. and 67° F.

§ 14. GENERAL UTILITY OF DECREMENT OBSERVATIONS

I find it difficult to understand why references to decrement experiments are so rarely to be found. In this way an accurate value can be found for the rate at which a pendulum dissipates energy, yet we find Denison[9] (later Lord Grimthorpe) equating this to the input by the driving weight—thus saddling the pendulum with train friction and deducing a value two or three times too large.

By decrement observations losses can be compared, for example, under different conditions of air and enclosure and different kinds of suspension and bracketing. By comparing decrements of long and short pendulums (using the same bob and spring) and of bobless pendulums of different lengths, I have found the contributions which bob, rod and suspension make to the total loss of energy. The result may have some bearing on the question whether long or short pendulums make the better timekeepers.

§ 15. TEMPERATURE AND STRATIFICATION

Temperature is read to 0·1° F. on a thermometer whose bulb is 2 cm. above the bob and on another one 67 cm. higher up. During the experiment the mean of consecutive morning readings of the lower thermometer was used for the compensation-correction for the intervening interval. Of course, this mean is not the average for the day, since the temperature goes through a cycle of changes in the time: the only defence for using it is based on the assumption that it was about as much below the average one day as another during the time of the experiment.*

* Since November, 1934, temperature has been recorded thrice daily.

The amount by which the reading of the top thermometer exceeds that of the other is a measure of Stratification. In a sealed case this is never absent and it has important effects on rate. Compensation in the region of the bob corrects for change of length of rod and change of elasticity of the spring. Increase of the temperature-gradient reduces the compensation. Moreover, the air-density increases below the centre of the case at the expense of the air-density higher up, and this slows the rate.

I am surprised that more attention is not given to stratification for precision clocks. I believe these are not always provided with the means of measuring it. It is often supposed that a fan used to blow warm air on to a case (usually bracketed to a wall or pillar cooler than the air) will prevent stratification inside.

§ 16. PRECISION WORK WITHOUT CONTROLLED TEMPERATURE

It will be noticed that this experiment was made with a clock whose temperature was not controlled (actually it varied by 11° F.). After experimenting with a Riefflер pendulum, Sampson states that "the correction of the mechanism of a clock for changes of temperature is, for fine work, a delusion"[11]. Results obtained with my pendulums between 1927 and 1931 pointed to a similar conclusion. Then in 1931 to 1933 I tried two pendulums in which the relation between rate and temperature was simpler, but it was necessary to allow for lag: the rate was higher for a rising temperature than for a falling one, apart from any correction for incomplete compensation. Finally, with pendulum 11 (used for this experiment) and pendulum 14 (under test in 1935) I cannot detect lag: it is sufficient to correct for over-compensation and stratification.*

Table 4.† Rate reduction (milliseconds per day)

Period	Observed	Greenwich	Compensation	Stratification	Acceleration	Barometer	Reduced
1	157	−3	− 50	−1	−41	+ 6	68
2	697	−4	− 50	+1	−45	+ 1	600
3	1100	0	− 54	0	−48	+24	1022
4	1517	+4	−131	−3	−52	− 4	1331
5	−567	+4	− 96	−3	−57	− 4	−723
6	108	−5	−108	−1	−60	−14	− 80
7	170	−6	−113	−1	−63	+25	12
8	365	0	−138	−1	−66	−18	142

† Observed rates by comparison with 10-h. signal; Greenwich corrections from *Notices to Mariners*; compensation reduced to 56·8° F. at −0·012 sec./day per ° F.; stratification reduced to 2·0° F. at +0·013 sec./day per ° F.; acceleration reduced to Jan. 1, 1934, at 0·0005 sec./day²; barometer reduced to 22·30 inches at 0·4 sec./day per inch.

§ 17. REDUCTION OF RATES TO STANDARD CONDITIONS

Table 4 shows the corrections applied to the observed rates to obtain the rates under standard conditions. The corrections to the Greenwich signals[10] are estimated after subsequent transit observations have indicated the general trend

* As regards pendulum 11, the evidence for this was accumulated during runs of 2½ months before the amplitude experiment and 8 months after it.

of the observatory clock rates. Stratification ranges from 0·5° F. in summer to 2·5° or even 3° F. in winter. It has only a small effect on the experiment as it ranged near to 2·0° F. all the time. The basic rate is assumed to have accelerated by 0·025 sec./day during the experiment. This is in accordance with observation during 2½ months before the experiment and fits in with earlier and later determinations in the 40 min. region. After May, however, the acceleration had disappeared. An aneroid barometer is not a very satisfactory instrument for measuring pressure in a case: when pressure is rising with temperature, friction (which cannot be overcome by tapping) gives a low reading, and *vice versa*. Further, after being at atmospheric pressure, the barometer approaches true readings for lower pressures slowly, so that several days are needed to ascertain the proper barometric correction to rate.

§ 18. NOTE ADDED FEBRUARY 7, 1936

Dr Max Schuler's[13] experiences with pendulums supported on knife-edges show that it is necessary to distinguish between the material knife-edge and the ideal* one referred to in § 1. The latter consists of two surfaces cutting in a straight line about which the pendulum turns. The material edge is part of a cylinder rolling on a supporting cylinder. As the pendulum swings to the right the point of contact moves to the left, thus the arm of the restoring moment is increased and the frequency with it[12].

ρ_0, θ (*a*) When a right circular cylinder of radius r_0 rolls in another one of radius R_0 the extra arm is almost exactly $\rho_0 \sin\theta$ where $\rho_0 = R_0 r_0/(R_0 - r_0)$. In this case the principal term of the circular deviation is unchanged (see § 1).

(*b*) If however ρ increases with θ, as when $\rho = \rho_0 + b\theta^2$, the extra arm increases faster than $\sin\theta$, and amplitude deviation is consequently less than circular deviation.

d When $b = \frac{1}{2}(d + \rho_0)$, where d is the distance of the edge from the centre of gravity, the principal term of circular deviation is balanced out and the pendulum is nearly isochronous.

(*c*) A slight bend in the cylindrical edge makes it behave as if the central part were flat, so that the edge rocks over suddenly from one boundary of the flat to the other as the pendulum passes the vertical, producing a relatively large restoring moment for small values of θ, so that there is a rapid increase in frequency as small amplitudes decrease: see branch OA, figure 4.

Since these material edges are minute—say between 0·001 and 0·0001 in. in width—ρ_0/d is usually quite negligible. It would be difficult to observe the shapes of such edges and quite impossible to produce desired forms.

Figure 4 shows the result of observations made in 1930 by G. Th. Gengler in Dr Schuler's laboratory. The dotted line represents circular deviation and the full line the excess of amplitude deviation over this. Thus for 30 min. the amplitude

* Ideal is not here used as suggesting a quality to be desired as improving the time-keeping of a pendulum.

deviation $= 0{\cdot}95 + 0{\cdot}41 = 1{\cdot}36$ sec./day. The test was repeated in 1933 by H. Gräfe[14] who found that the deviation was unchanged, indicating that the knife-edge and support had resisted wear. This cylindrical edge either has a flattish face which makes contact with the support when $\theta \fallingdotseq 0$, or more probably it is slightly bent.

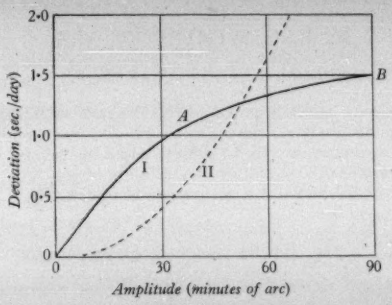

Figure 4. Deviations of Schuler pendulum with knife-edge suspension. I, Excess of amplitude deviation over circular deviation; II, circular deviation.

Such observations have been analysed by H. Gebelein[15], who has furnished a mathematical theory.

We thus reach this striking conclusion: although a spring-suspended pendulum can behave as if supported by an ideal knife-edge, a pendulum with a material edge has little chance of doing so.

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DISCUSSION

See page 621.

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ON AIRY'S DISTURBANCE INTEGRALS AND KNIFE-EDGE SUPPORTS FOR PENDULUMS

By E. C. ATKINSON, M.A.

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ABSTRACT. A century ago Airy employed two integrals to find the effect of a small disturbance on harmonic motion. More general use of these would have saved much effort in theoretical investigations. In the present paper the process is used to find the effect of a material knife-edge, consisting of a cylinder of any form rolling on another supporting cylinder, on the period and isochronism of a pendulum.

§ 1. THE DISTURBANCE INTEGRALS

In 1827 G. B. Airy[1] (afterwards Astronomer Royal) expressed the effect of a small disturbance of harmonic motion, which produces angular oscillation $\pi\sigma$ when the displacement is θ, in terms of two integrals $\int_0^{2\pi}\sigma\cos\tau\,d\tau$ and $\int_0^{2\pi}\sigma\sin\tau\,d\tau$ relating respectively to change of amplitude α and of frequency $n/2\pi$. τ is the phase of vibration: $\sin\tau=\theta/\alpha$. These integrals were used by Airy and by Denison[2] (Lord Grimthorpe) and more recently by Sampson[3] and David Robertson[4] in connexion with clock pendulums.

σ

θ

α, n, τ

§ 2. SHOULD BE BETTER KNOWN

Much time and energy would be saved if these useful mathematical weapons were more generally recognized as such. Thus Bloxam[5], whose gravity escapement was used for the clock of the Houses of Parliament, wrote in 1853 on the theory of this escapement and of the dead-beat. He devised ingenious ways of getting his results at the expense of unnecessary labour to himself and to his readers.

By free use of Airy's method the second volume of Grossmann's[6] monumental *Horlogerie Théorique* could have been transformed. Not only would the analysis have been simplified but some of the results whose present form is so complex that the meaning can only be brought out by numerical examples would have automatically appeared in simple garb. Krebs[6] deals with the poising error of a balance wheel which is obtained as the sum of an infinite number of series. He gives only the outline of the reduction of this sum to the final series, yet this outline needs four pages. The Airy Integral $\frac{gh}{2\pi n^2k^2\alpha}\int_0^{2\pi}\sin\theta\sin\tau\,d\tau$ gives the result in a single line.

Gebelein[7] has dealt with the behaviour of a pendulum rolling on a so-called knife-edge. He reaches the general case in six stages occupying seventeen pages. All goes well until an error in the work of stage 5 makes the final formulae incorrect. The Airy solution is given in § 4 of this paper.

§ 3. EXAMPLE: CIRCULAR DEVIATION

I have discussed these functions elsewhere[8], but will show the use of the second one to obtain a result needed here. The simple equation of pendulum motion is

$$(d^2+k^2)\,\ddot{\theta} = -g\,d\,\theta, \qquad g$$

leading to

$$n = \sqrt{\frac{gd}{d^2+k^2}} \qquad \text{.....(1),}$$

mk^2 being moment of inertia about the centre of mass and d the distance from this point to the axis. For finite amplitudes, the restoring moment is $mgd\sin\theta$, so there is a correcting term to $(d^2+k^2)\,\ddot{\theta}$, namely $g\,d\,\theta^3/6$. m, k, d

$$\therefore \quad \pi\sigma = \frac{g\,d\,\theta^3}{6\,(d^2+k^2)}.$$

The Airy formula gives

$$\frac{dn}{n} = -\frac{1}{2n^2\alpha}\int_0^{2\pi}\sigma\sin\tau\,d\tau = -\frac{1}{12\pi\alpha}\int_0^{2\pi}\alpha^3\sin^3\tau\sin\tau\,d\tau = -\frac{\alpha^2}{16} \qquad \text{.....(2).}$$

§ 4. THE MATERIAL KNIFE-EDGE

The ideal knife-edge is a straight line forming an axis. The material edge is some form of cylinder rolling on another cylinder which supports it. Schuler[9] found that rate changed with amplitude, when pendulums were supported on edges, by no means according to circular law given in equation (2). Hence Gebelein's investigation.

Whilst the pendulum swings through θ to the left, the edge rolls to the position $O'A$ making contact with its support at A so that the arcs $O'A$ and OA are both equal to s. s

If r and R are the radii of curvature at A of edge and support respectively r, R

$$Rd\phi = ds = r\,(d\phi + d\theta). \qquad \phi$$

$$\therefore \quad d\phi = rd\theta/(R-r) \qquad \text{and} \qquad ds = \frac{Rr}{R-r}\,d\theta = \rho\,d\theta, \text{ (say)} \qquad \rho$$

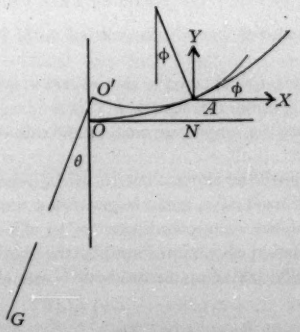

Figure 1.

Quantities of higher order (§ 6) being neglected, the equation of motion becomes

$$(d^2+k^2)\,\ddot{\theta} = -g\,(d\sin\theta + s) \qquad \text{.....(3).}$$

ρ_0, s_0 (*a*) If ρ everywhere $=\rho_0$, $s_0=\rho_0\theta$.

n_1
$$\therefore\quad n_1 = \sqrt{\frac{g\,(d+\rho_0)}{d^2+k^2}}\cdot\left(1-\frac{\alpha^2}{16}\right) \qquad \text{.....(4).}$$

In this case the rate is changed by the circular shape of the edge, but, if the small quantity $\rho_0\alpha^2/32d$ is neglected, the circular deviation is unchanged.

(*b*) If r and R are variable, s is larger than in (*a*) by $s-s_0$

$$\frac{dn}{n_1} = \frac{g}{2\pi n_1{}^2\,(d^2+k^2)\,\alpha}\int_0^{2\pi}(s-s_0)\sin\tau\,d\tau = \frac{4}{2\pi\,(d+\rho_0)\,\alpha}\int_0^{\frac{\pi}{2}}\cos\tau d\,(s-s_0)$$

$$= \frac{2}{\pi\,(d+\rho_0)}\int_0^{\alpha}(\rho-\rho_0)\cos\tau\,\frac{d\theta}{\alpha} \qquad \text{.....(5).}$$

This result is obtained by integration by parts and corresponds to Gebelein's equation (34).

§ 5. FORM FOR ISOCHRONISM

b Suppose $\qquad \rho=\rho_0+b\theta^2, \quad \therefore\ s=s_0+b\,\theta^3/3.$

Then
$$\frac{dn}{n_1} = \frac{2b}{\pi\,(d+\rho_0)\,\alpha}\int_0^{\frac{\pi}{2}}\frac{\theta^3}{3}\sin\tau\,d\tau = \frac{b\alpha^2}{g\,(d+\rho_0)},\ \text{as in § 3,}$$

$$n = \sqrt{\frac{g\,(d+\rho_0)}{d^2+k^2}}\cdot\left\{1-\left(1-\frac{2b}{d+\rho_0}\right)\frac{\alpha^2}{16}\right\} \qquad \text{.....(6).}$$

Here the growth of ρ with θ reduces the circular deviation. When $b=\frac{1}{2}\,(d+\rho_0)$ the pendulum is nearly isochronous.

§ 6. EFFECT OF NEGLECTED TERMS

In equation (3) quantities have been omitted as of higher order than those retained.

To estimate this order, I shall take the special case in which $R=\infty$ and suppose that $d=100$ cm. With R finite, s in equation (3) is too large by a quantity of order $s\theta^2$ or say 4×10^{-4} of itself for amplitude 0·02, i.e. 68 min. of arc. For isochronism $b=50$ cm., $b\alpha^2=0{\cdot}02$.

If $r_0=0{\cdot}06$, the edge will be about 0·002 in. wide, larger, I think, than is likely to be the case. This will make all r_0 terms larger than b terms and I use the former only in finding order of size. The coordinates (x, y) of O' are easily found to be $(r_0\theta^3/6,\ r_0\theta^2/2)$. The equation of motion found by the routine method of resolving vertically and horizontally, taking moments about G and eliminating X and Y, is

$$-(d^2+k^2)\,\ddot{\theta} = (g+\ \dots\ +\ddot{y})\,(d\,\theta+\ \dots\ -x)+(d\,\ddot{\theta}+\ \dots\ -\ddot{x})\,(d+\ \dots\ -y)$$

$$= -g\,x+d\,\ddot{y}\,\theta-d\,y\,\theta-d\,\ddot{x}+\ \dots$$

where the omitted terms are introduced and the largest of the old ones retained,

$$d\,y\,\ddot{\theta} = d\,r_0\,\theta^2\ddot{\theta} = 100 \times 0{\cdot}06 \times \tfrac{1}{2}\,(0{\cdot}02)^2 \times n^2\,(0{\cdot}02) = 2{\cdot}4 \times 10^{-4} \text{ since } n^2 \doteqdot 10,$$

similarly for the other terms. All are of order 10^{-4}, whereas the principal term $gd\,\theta$ is of order 10^{3}, the circular deviation term $gd\,\theta^3/6$ of order 10^{-1}, and gs between 1 and 10^{-1}. Thus the small term given by equation (5) may be regarded as correct to 1 in 1000 for a normal edge.

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DISCUSSION OF THE PRECEDING TWO PAPERS

Sir C. V. Boys wished that the author, who made his own instruments with beautiful workmanship, could work 50 ft. below ground so as to obtain a steady temperature without stratification. A thermostat could never be completely effective because it can only act when a slight change of temperature occurs and the parts of the pendulum take some time to adjust themselves to the slight change; moreover stratification results. At Greenwich it would be possible to drive a hole under the hill and above the river-level without disturbing the transit instruments, but the author lived on clay soil so that he could not conveniently construct an underground laboratory.

Dr G. A. Tomlinson. The experimental results given in table 2 appear to me to prove that the mathematical correction applied on account of the impulse deviation is justified. This correction is a large one and amounts to more than twice the observed changes of rate. The author defines amplitude as the maximum inclination of the pendulum to its free rest position, and the elastic energy of the suspension is therefore strictly proportional to amplitude. The suspension should thus introduce no appreciable deviation from isochronism, leaving only impulse and circular deviations as possible causes of change of rate of the first order. The close agreement with the theoretical values of circular deviation, after a theoretical allowance $86{,}400\ \delta \cot \tau/2\tau f$ for the impulse deviation, is an experimental demonstration of the validity of this expression as applied to this particular system of impulsing.

The close agreement the author has obtained in such short trials as these, lasting 4 days in certain cases, suggests that he has an efficient way of comparing the clock

with the rhythmic signals, and I should be pleased to learn what method of observation he uses.

Prof. POLLARD. Recently I have endeavoured to determine the shape and curvature of knife-edges and in the course of devising methods I have obtained some information which might interest Dr Schuler and Mr Atkinson. I have naturally tried out the methods with the finest agate balance edges I could obtain and have found that they all, with the exception of one particularly fine microbalance agate, contact with an optical flat at one or at the most two portions of their whole length. This can easily be seen under the microscope by the system of interference fringes formed in the neighbourhood of the edge.

The cylindric surface of the edge is fortuitously formed by the meet of two facets and if this fortuitous surface is to touch a plane along its whole length obviously the facets must be true planes. The facets of all the agates considerably deviate from plane surfaces, except those of the microbalance agate. In this agate the facets, 8 mm. long and averaging 0·02 mm. wide, approximate to optical flats and consequently the cylindric edge touches an optical-flat along its whole length. The contact, however, is localized along the cylindric surface at numerous short lengths separated by fractures and other imperfections. The ratio of the contacting length to the whole length is important in so far as the permissible loading is concerned. But the measurement of this would be very tedious since a magnification of at least 360 diameters is necessary to observe the minute fringe system in monochromatic light. If a cylindrical planoconvex lens of radius 0·068 mm. is placed perpendicular to the edge of this agate and nearly touching it, the ratio of the principal axes of the elliptic fringe pattern indicates that the radius of curvature is about 3 μ., and from the regularity of the fringe pattern with an optical flat it might be supposed that the cylindric surface does not differ very much from that of a circular cylinder. I find that by tilting the optical flat at a small angle to the length of the edge the fringe pattern can easily be seen under the microscope, but I have not had an opportunity of photographing it and obtaining the true shape of the edge by geometrical projection. Some edges that I have examined by these methods are so imperfect that it is difficult to imagine how they would roll on a plane surface.

When the edge is loaded in contact with its bearing, both surfaces will deform into a common surface the shape and breadth of which will depend upon the elastic constants as well as the load, but the limiting load before permanent deformation takes place depends upon the Hertzian hardness. Since agate is crypto-crystalline it is probable that the Hertzian hardness rather than the elastic constants will vary over the common surface; it will certainly vary when the material is steel unless extraordinary precautions are taken in the hardening processes. The common surface will be complex especially in the neighbourhood of the fractures in the case of agate, and in the case of steel it may be permanently deformed locally if the loading is too high. It is evident then that the permissible loading for a knife-edge depends upon the Hertzian hardness, and a method of measuring this for non-brittle materials is described in a paper which I am endeavouring to publish. Presumably

a steel edge will cold-work with use into an unalterable surface condition with greatly increased Hertzian hardness and this may be the explanation of the resistance to wear observed by Gräfe. The super-hardening of steel by cold work is well known and has been applied by E. G. Herbert* in his cloud-burst treatment of steel. As far as I am aware the correct design of a knife-edge bearing has never been fully considered.

The fixing of the knife-edge to the pendulum requires as much care as its construction if the bending referred to by Mr Atkinson is to be avoided. The knife-edge is usually in the form of a triangular prism and is generally force-fitted into a dove-tail groove. The prism is thus held in position by the indeterminate contact of ordinary engineering functional surfaces and is more likely than not to be subjected to unknown bending moments.

The correct way to fix the prism is to work its base as well as the mating surface on the pendulum to optical flatness. The prism can then be wrung into position on the mating surface with the assurance that all parts of the two surfaces are in contact. The prism may be retained in position in a state of repose by four screws which abut normally upon the sloping surfaces in pairs directly opposite one another. With these precautions the prism cannot be subjected to bending moments, provided no part of it overhangs and the plane of pressure never passes outside its base when the pendulum swings through its maximum amplitude.

Prof. MAX SCHULER (communicated). In the note added February 7, 1936 the author mentions my experiments upon the dependence of the rate on the amplitude of pendulums supported on knife-edges. He has rightly insisted that my experiments show the necessity for distinguishing carefully between the material and the ideal knife-edges. The relation between amplitude and rate is different in the two cases. The ideal knife-edge is a mathematical line, and in this case amplitude deviation is circular deviation. The material knife-edge, on the other hand, is a cylinder of very small radius of curvature rolling on a plane. As this radius, obtained by grinding, has no constant value, amplitude deviation can be determined only by experiment. The shape of the edge can be approximately calculated from the observed deviation.

In my opinion the best edge is not the one which approaches the mathematical line, but that which has the smallest coefficient of friction. A rolling cylinder with a finite radius will reduce undue strain of the materials and consequently permanent deformation and wear are countered. For these reasons I selected for my experiments a knife-edge with very little friction. The logarithmic decrement of the pendulum was only $0{\cdot}127 . 10^{-4}$ per second and this value remained constant between 100′ and 1′ of amplitude.

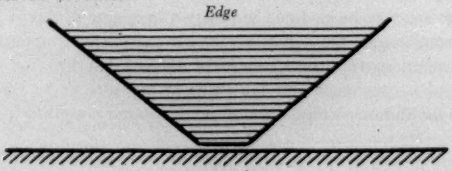
The weight of the pendulum was 8800 g. The case was filled with hydrogen and the pressure was 200 mm. of mercury. The knife-edge is of hardened steel and rests on a polished agate surface. The angle of the knife-edge is 100° and the weight it carries is 4·4 kg. per cm. With this knife-edge the amplitude deviation

* *Trans. Amer. Soc. for Steel Treating*, **14**, 680 (1928).

was quite different from the circular deviation. From this it follows that the edge is not quite sharp but somewhat flattened, as shown, very much exaggerated, in the illustration. The author's assumption that the knife-edge was not absolutely straight is wrong.

I purposely selected this flattened knife-edge in order to ascertain whether the amplitude deviation of the rate would change in the course of time through grinding of the surfaces. Gräfe's experiments, however, proved that the amplitude deviation had not changed after the pendulum had been in use for three years. The knife-edge had, therefore, not altered during this period and no effect of wear is yet observable.

Very exact observations of the deviation could be made, for these were taken on the free pendulum with the electrical impulse cut off. I was thus able to eliminate impulse errors which, as the author says, were responsible for by far the largest errors in his measurements. The measurement was accurate to about 1 per cent of the observed deviation.



If the author were to conclude that a pendulum suspended by a spring is better for time-keeping purposes than one supported by a knife-edge, I could not agree with him. The rate should be a single-valued function of the amplitude. This function must not alter in the course of time. That such a function is possible I have proved experimentally. It is not important for the result whether the amplitude deviation equals circular deviation as calculated by the mathematician for the circular pendulum. It is possible to produce knife-edges for which the difference between amplitude deviation and circular deviation is much smaller than with those I have employed. I did not consider this of any importance and I evolved my knife-edge according to my conception of the best form. No other pendulum time-keeper has shown results as good as those obtained with my pendulum supported on a knife-edge. The results of relative gravity measurements with knife-edge-supported pendulums confirm my opinion. For such purposes knife-edge-supported pendulums are to-day used with very accurate results.

My study of the subject leads me to the conclusion that the makers of astronomical standard clocks will, in the near future, employ this knife-edge support exclusively.

Author's reply. Sir Charles Boys naturally wishes the pendulums at Greenwich to enjoy the steady underground temperature which has been secured for the astronomical clocks at Paris. Yet I am not certain that an invariable temperature is the best thing for invar rods. Observations made at Greenwich, Yale and Göttingen under thermostatic control suggest that abrupt changes of rate occur

more readily under these conditions than when pendulum temperature is constantly changing (see also § 16). On the other hand, Shortt 44 in Paris during 1935 was free from changes which could be attributed to invar: such changes as did occur were purely erratic.

Dr Tomlinson is not justified in assuming that the suspension "introduces no appreciable deviation from isochronism" until Sampson's equations have been solved without rejecting squares and higher powers of the displacement. The spring complicates matters not only by supplementing the restoring couple due to gravity but also by modifying the path of the centre of gravity of the pendulum. Dr Tomlinson has surely overlooked air resistance and air inertia as possible causes of deviation when he speaks of impulse and circular deviation as the only causes left for change of rate. If all the matters referred to in § 2 could be decided without recourse to experiment, I should agree that my experiment would be simply a test of the correctness of the formula for impulse deviation.

During the 5 minutes' transmission of rhythmic signals there are five coincidences. I attempt to estimate to the nearest half-second and when in doubt I avail myself of all the coincidences. Precision is reduced by atmospherics and other disturbing noises and is increased by the cleanness and brevity of the two signals. In the early days of the Rugby transmission the Greenwich dots were far too long and inferior in this respect to the Paris signals. There has been improvement, but still shorter signals are much to be desired.

My earliest apparatus had a low-resistance earpiece for the clock signal and a high-resistance one for the wireless signal. The latter sounded in the left ear, but one day the phones were accidentally reversed so that the left ear, accustomed to a signal overtaking the other before coincidence, found itself listening to a signal ahead of the other. I could not avoid concluding that the coincidence was already past and was quite unable to make an observation.

Prof. Pollard's studies of knife-edges are of great interest. The optical method gives a measure of the mean radius of curvature, whilst the pendulum deviation indicates how this varies from point to point. I hope that Prof. Pollard will soon be able to determine the form of the edge. The elastic deformation, due to loading, probably modifies the pendulum deviation to an appreciable extent. Both Gebelein and I assume the edge and the supporting surface to be rigid, so the results must be regarded as first approximations. I conclude that a pendulum with a good knife-edge correctly attached is at present a rarity. The attaching of a good suspension spring is not a formidable task, but the making of it is another matter. I hope some day to accomplish this with more certainty than at present.

Dr Schuler is in favour of using knife-edges for supporting pendulums, believing that better timekeeping is secured in this way than with suspension springs. Gräfe's observations indicate good rate-holding quality for an edge, but I have not yet seen records of timekeeping with the Schuler pendulum which encourage the expectation that the knife-edge will replace the suspension spring. In a future paper I hope to describe experiments dealing with the capacity of different pendulums to maintain a constant rate.

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ABSORPTION SPECTRA AND PHOTODISSOCIATION OF SOME INORGANIC MOLECULES

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ABSTRACT. The absorption spectra of PCl_3, PBr_3, PCl_5, PBr_5, $POCl_3$, P_2O_5, $AsCl_3$, $SbCl_3$, SbOCl, and $BiCl_3$, are investigated. The regions of selective absorption are correlated to certain photodissociation processes. A comparison with the mean bond energies as known from thermochemical measurements, allows certain conclusions to be drawn as to the structure of these molecules.

§ 1. INTRODUCTION

Continuous absorption spectra of polyatomic molecules have been investigated recently by a number of authors. The following work was undertaken in order to supplement the results obtained by Butkow[1] and Trivedi[2] for molecules formed by the fifth-group atoms P, As, Sb, and Bi, and so derive some general rules about the photodissociation of more complex inorganic molecules. The spectra of SbI_3, $BiBr_3$, and BiI_3 as measured by Butkow show a definite structure and several maxima in each case, whereas Trivedi has found a long-wave limit only. This difference leads to a fundamental difficulty which must be discussed at the outset. A continuous absorption spectrum means a process of photodissociation, i.e. a transition from the stable ground state of the molecule to a repulsive curve in the Franck-Condon diagram. A comparison of the long-wave limit with bond energies calculated from thermochemical measurements is possible, however, only if this long-wave limit really represents the transition to the repulsive curve from the vibrationless ground state. As soon as the population of the higher vibrational levels of the ground state is increased so that these higher levels influence the absorption spectrum, the long-wave limit shifts towards longer wave-lengths, because the energy difference between the higher levels and the repulsive curve is smaller. This effect is the more marked, the steeper the slope of the repulsive curve. In fact, by increasing the population of the higher vibrational terms, either by increasing the absolute number of molecules under investigation by longer absorption tubes or by increasing the percentage of molecules with excited vibrational levels by increasing the temperature of the gas or vapour, it is experimentally possible to shift the long-wave limit towards longer wave-lengths inside very wide limits. The original investigations of Franck and his collaborators were concerned with the alkali halides in which the repulsive curve is rather flat owing to Van der Waals forces between the non-ionized atoms in their respective ground

states, and the agreement between the optical and thermochemical measurements was very good. Subsequently this feature of the continuous absorption spectra has been sometimes overlooked. This has led to some attempts to prove the ionic nature of the bonds of the hydro-halides in the gaseous state by shifting the long-wave limit to smaller energy values, whereas the Raman effect, the electric conductivity and the dipole moment establish the bond as that of a covalent dipole molecule[3]; or, in cases like methyl iodide, where the absorption spectrum yields a value far above the thermochemical one on account of the steepness of the repulsive curve, attempts have been made to diminish the optical value, again by shifting the long-wave limit artificially towards smaller energy values[4]. We think such attempts are misleading, since only the transition from the vibrationless ground state of the molecule has a good physical meaning for comparison with thermochemical bond energies. There remains, however, the difficulty of deciding which of the many possible values of the long-wave limit corresponds to this transition. According to the Beer-Lambert law the absorption of the vibrationless molecule can be represented by a curve connecting wave-length and the number of molecules. Hence, if the number of molecules is not big enough, e.g. if the vapour pressure is too low, the long-wave part of the curve will not be reached at all and the determined energy of the long-wave limit will be far too high. If, on the other hand, the number of molecules is too big, the number of molecules in higher vibrational levels is also increased, and the measured energy of the long-wave limit is far too low (cf. figures 2 to 5). The decision is easier if the continuous absorption spectrum shows in the region investigated a structure, which indicates definitely the part of the absorption curve really measured. The greater the excitation of higher vibrational levels, the more broadened the absorption regions become. As can be seen from the Franck-Condon curve, transitions from higher levels and bigger internuclear distance broaden each maximum towards longer wave-lengths, those from the same levels and smaller internuclear distance produce the same effect towards shorter wave-lengths. The different regions of selective absorption, therefore, ultimately merge into one continuous spectrum without any structure. Consequently the value of the long-wave limit in a spectrum still showing distinct maxima and minima will be nearer to the true value for the vibrationless molecule. Wherever possible, i.e. wherever the maxima appear in the region investigated, only such values should be taken into account. Accordingly we have measured the absorption spectra of several molecules, formed by atoms of the fifth group, including some for which only the long-wave limit was determined by previous workers. The spectra of the following substances have been taken: PCl_3, PBr_3, PCl_5, PBr_5, $POCl_3$, P_2O_5, $AsCl_3$, $SbCl_3$, SbOCl, and $BiCl_3$.

§ 2. EXPERIMENTAL

As absorption cells, tubes of fused silica of 5, 10 and 20 cm. long, connected with the usual vacuum arrangement and manometer, were used. In the case of liquids the substances were contained in a side bulb and the vapour introduced in the apparatus after repeated evacuation and thorough washing of the absorption

Figure 1. Upper curve = absorption of PBr_3, absorption cell 1 cm. length, vapour pressure = 4 mm. Lower curve = source of light.

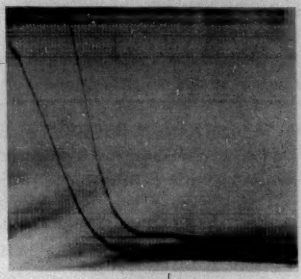

Figure 2. Upper curve = absorption of $SbCl_3$, absorption cell 10 cm. length, 61° C. Lower curve = source of light.

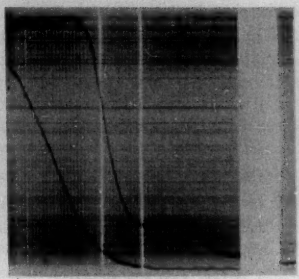

Figure 3. Upper curve = absorption of $SbCl_3$, absorption cell 10 cm., length, 72° C. Lower curve = source of light.

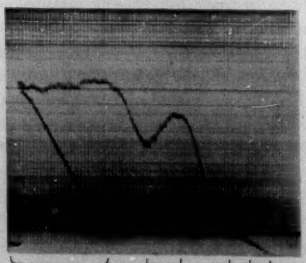

Figure 4. Upper curve = absorption of $SbCl_3$, absorption cell 10 cm., length, 84° C. Lower curve = source of light.

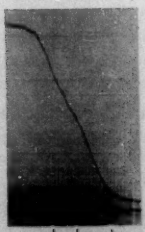

Figure 5. Upper curve = absorption of $SbCl_3$, absorption cell 10 cm., length, 130° C. Lower curve = source of light.

cell by the vapour itself. During longer exposures the vapour was frequently renewed. Solids were introduced in the absorption cell itself in small quantities and the cell heated either by an electric stove or, if there was danger of decomposition, by a current of warm air. The H_2 continuous spectrum was used as a source, Cu arc lines as standards, and the Hilger medium quartz spectrograph as the resolving instrument. The density of the spectra was measured on the recording microphotometer, the long-wave limits and the positions of the absorption maxima were determined from the photometer plates, of which figures 1 to 5 are typical.

Phosphorus tribromide. The spectrum of PBr_3 at 4 and 5 mm. vapour pressures in a 5 cm. tube shows complete absorption to about λ 3200 and λ 2450 respectively, and at 4 mm. pressure in a 1 cm. tube, to λ 2360. The photometer plate of the latter shows two flat maxima at λ 2695·5, ν 37088 and λ 2495, ν 40068 (see figure 1), with an energy difference of 0·37 V. The corresponding long-wave limits are λ 3082·5, ν 32432 and λ 2635·0, ν 37939 respectively; the third long-wave limit (following the second maximum) is not very well defined but lies at about λ 2440, ν 40971. Thus the absorption due to the first maximum covers a region of about 5500 $cm.^{-1}$, that due to the second about 2000 $cm.^{-1}$ only. Hence the first (lower) of the two repulsive curves is the steeper, and the energy difference between them will be slightly less than the real difference between the separated systems. Since the term difference $^2P_{\frac{1}{2}}-{}^2P_{\frac{3}{2}}$ of the Br atom is 3685 $cm.^{-1}$ or 0·38 V., i.e. slightly greater than that between the two maxima, the two dissociation processes are probably

$$PBr_3 \rightarrow PBr_2 + Br(^2P_{\frac{3}{2}})$$

and

$$PBr_3 \rightarrow PBr_2 + Br(^2P_{\frac{1}{2}}).$$

The third region at shorter wave-length will probably have an excited —PBr_2 radical as one of its products. The first long-wave limit λ 3082·5 gives 92·0 kcal./mol. for the photodissociation of PBr_3 in its ground state; the values of the other two long-wave limits are 108·1 and 116·2 kcal./mol. respectively.

Phosphorus trichloride. The continuous absorption of PCl_3 is slightly less liable to changes with increase of pressure; this may be due to an increased spacing of the vibrational levels of the ground state. The beginnings of complete absorption in a 10 cm. tube are roughly as follows:

Pressure (mm.):	3·5	8	18	40	60
λ (A.):	2410	2440	2460	2490	2520

No maxima could be observed on the photometer plates, probably because they are at shorter wave-lengths than in PBr_3. Trivedi[2] obtained λ 2957 as the long-wave limit (tube-length and pressure not mentioned, probably high) while the microphotogram of the second of the above spectra revealed a value of λ 2815·5, ν 35507 or 101·2 kcal./mol.

Phosphorus pentabromide. The spectrum of PBr_5 shows Br_2 absorption bands clearly at 55° C. and fully developed at 72° C.; lower temperatures and corresponding vapour pressures had, therefore, to be used. With 4 mm. pressure and a 10 cm. cell the spectrum shows a maximum at λ 2744, ν 36432, and retransmission

occurs at λ 2688, ν 37191 or 105·1 kcal./mol.; the first long-wave limit is λ 3146, ν 31777 or 99·0 kcal./mol. The extent of this first region of selective absorption indicates again a steep repulsive curve. A correlation of the two regions of absorption with particular processes of photodissociation is not possible, since the second maximum could not be determined and the energy difference of the long-wave limits themselves depends too much on experimental conditions to be used with safety.

Phosphorus pentachloride. The spectrum of PCl_5 indicates decomposition (Cl_2 absorption) at about 80° C. upwards. At about 25° C. (room temperature) and 6 mm. pressure complete absorption occurs from λ 2130 onwards. The plates chosen for final measurement were taken up to 55° C. and 10 mm., under which conditions the absorption spectrum seems fully developed. As in the case of PBr_5, one single maximum was obtained at λ 2310, ν 43277; the two long-wave limits are λ 2240, ν 44629 or 126·7 kcal./mol. and λ 2625, ν 38084 or 108·1 kcal./mol. The extent of about 6500 $cm.^{-1}$ indicates again a steep repulsive curve.

Phosphorus pentoxide shows a spectrum with continuous end-absorption only; no maximum was found. At 450° C. in a 10 cm. cell the absorption is complete from λ 2200 onwards, and at 563° C. (the melting point) from λ 2400. The corresponding long-wave limits are λ 2270, ν 44039 or 124·9 kcal./mol. and λ 2530, ν 39514 or 112·0 kcal./mol. respectively.

Phosphorus oxychloride. The spectrum of $POCl_3$ at 3·5 cm. vapour pressure in a 20 cm. cell shows complete absorption from λ 2200, and a long-wave limit at λ 2250, ν 44431 or 126·0 kcal./mol. With reduced pressure no maximum could be detected on a Schumann plate down to about λ 1900.

Arsenic trichloride. Complete absorption obtains in $AsCl_3$ at about 25° C. in a 10 cm. cell from about λ 2390 onwards at 2 mm. vapour pressure, about λ 2420 at 6 mm. and about λ 2510 at 12 mm. Photometric measurements of the first of these spectra show one maximum at λ 2547, ν 39250; the preceding and following long-wave limits lie at λ 2687, ν 37205 or 105·6 kcal./mol. and λ 2475, ν 40392 or 114·8 kcal./mol. Trivedi[2] obtained a long-wave limit at λ 3466 or 82·1 kcal./mol., but no structure of the spectrum; we therefore believe our value to be the more accurate for the vibrationless molecule. According to the extent of the first region of absorption the repulsive curve seems to be again rather steep.

In $AsCl_3$, and in $SbCl_3$ and $BiCl_3$ (below), a correlation of the different regions to particular photodissociation processes is not possible at the present moment, since the Cl atom does not possess any low terms (besides the very small ^2P separation which cannot be recognized in such spectra) and those of the respective radicals are not yet known.

Antimony trichloride. The change of absorption with temperature and pressure can be seen from the following figures for the beginning of complete absorption in a 10 cm. cell:

Temperature (°C.):	25	61	72	84	130
Pressure (mm.):	0·5	2	2·5	3	12
λ (A.):	2190	2305	2350	2410	2620

The micro-photograms show a flat maximum at λ 2745, ν 36419, and a second very high and prominent maximum at λ 2551·5, ν 39181. The long-wave limits of the three regions of absorption are λ 2837, ν 35238 or 99·8 kcal./mol., λ 2694, ν 37109 or 105·3 kcal./mol., and λ 2475, ν 40392 or 114·8 kcal./mol. Trivedi[2] found λ 3256 or 87·3 kcal./mol. as the first long-wave limit, but no structure of the spectrum; our value appears to be the more accurate for the vibrationless molecule. According to the extents of the different regions of selective absorption the first repulsive curve is less steep, but the second one even slightly less steep as in $AsCl_3$.

Antimony oxychloride. Since this substance seems liable to decomposition when heated its spectrum is difficult to obtain. At 100° C. in a 10 cm. cell the long-wave limit was found at λ 2460, ν 40638 or 115·2 kcal./mol.; this energy may be still slightly too high on account of insufficient vapour pressure (about 4 mm.). No structure was observed.

Bismuth trichloride. The absorption by $BiCl_3$ in a 10 cm. absorption cell is complete from λ 2200 onwards at 90° C., from λ 2240 at 160° C., from λ 2370 at 240° C., from λ 3340 at 290° C., and from λ 4100 at 335° C. It shows a marked maximum at λ 2800, ν 35704, and the long-wave limits of the two regions of selective absorption lie at λ 3350, ν 29842 or 83·6 kcal./mol., and λ 2660, ν 37583 or 106·7 kcal./mol. The first repulsive curve appears to be rather steep. Trivedi[2] found the first long-wave limit at λ 3656 or 77·2 kcal./mol., but no structure; our value therefore seems to be the more accurate for the vibrationless molecule.

§ 3. THERMOCHEMICAL CALCULATIONS

In order to know more about the processes of photodissociation, we have to compare the energies so determined with the atomic energies of dissociation (D) of the molecules in question. Following Born and Haber's cycle we calculate this energy by adding to the heat of formation from the elements (Q) the energy necessary to convert the elements into gaseous atoms and (if Q refers to the liquid or solid state) deduct the heat of vaporization or sublimation of the compound. The energy necessary to transform a solid or liquid non-metallic element into its atoms in the gaseous state comprises the energy of sublimation (S) or of vaporization (L) alone, the energy of dissociation of the diatomic molecule (D), and, sometimes the energy necessary to split up a polymerized molecule like S_8 into diatomic molecules. Of these different energies S and L are more or less known for the elements, but only few measurements are available for the compounds. These quantities are small, however, compared with Q and D and may therefore be estimated by one of the known empirical rules; we have mostly used Walden's rule[5] for L and Forcrand's rule[6] for S; if T_m and T_b denote the melting and boiling points respectively (absolute temperatures), we have $L \doteq 13{\cdot}5\ T_m$ and $S \doteq 30\ T_b$. The heat of formation Q is mostly accurately measured. The energies of dissociation of the diatomic elements are determined spectroscopically; they can be determined with extreme accuracy, if a point of convergence is measured in the band spectrum and the products of dissociation are known; if, however, the

latter are doubtful, or if D is determined by linear extrapolation of the vibrational levels, the results are liable to later corrections. In the following we shall use other authors' results on the absorption spectra of polyatomic molecules in the vapour state, but a number of recent corrections of the dissociation energies of the diatomic molecules render necessary a recalculation of all the older data. The elements of interest for the following comparison are the halogens, nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur, and tellurium.

The spectra of the halogens show a convergence point; the dissociation products are an unexcited and an excited $^2P_{\frac{1}{2}}$ halogen atom; from these considerations D has been determined to be 56·9, 45·2, and 35·6 kcal./mol. for Cl_2, Br_2, and I_2 respectively[7]. For N_2, whose dissociation energy had been calculated to 207·5 kcal./mol. by linear extrapolation of the vibrational levels, a new value, $D = 169$ kcal./mol., taken from predissociation is now available[8]. The dissociation energy of P_2 has been determined from its predissociation as 115·5 kcal./mol. or 5·008 V.[9] For As_2, Sb_2, and Bi_2 no values are available; we have therefore estimated their dissociation energies as roughly 4, 3, and 2 V., using certain empirical rules obtained from band spectrum data[10]; these values, though not accurate, are believed to give the correct order of magnitude. In O_2 a convergence point is directly measured, but from its energy value the ^1D term value of O has to be deducted, giving $D = 117{\cdot}4$ kcal./mol.[11] The predissociation of S_2 yields a value $D = 102{\cdot}6$ kcal./mol. Rosen[12], who observed directly the convergence points in the spectra of S_2, Se_2, and Te_2 as 4·94, 3·81, and 3·22 V. respectively, believed the dissociation products to be an unexcited S atom and a S atom in a higher component of the ^3P ground state. Later investigation of the S_2 and Se_2 spectra have made it clear, however, that this analogy with the halogens is not correct; rather, as in O_2, the dissociation products of the upper $^3\Sigma$ level are $S(^3P) + S(^1D)$ etc. and hence the ^1D term value has to be deducted from the convergence point. Since these term values have recently been determined[13] as 1·14, 1·18, and 1·30 V. for S, Se, and Te respectively, new and more accurate values for the dissociation energies may be obtained in this way[14], namely 3·80 V. or 88·4 kcal./mol. for S_2, 2·63 V. or 59·3 kcal./mol. for Se_2, and 1·92 V. or 43·7 kcal./mol. for Te_2.

The definite values to convert elements which appear in thermochemical equations as solids or liquids, are obtained from the above dissociation energies by adding S or L respectively and, where necessary, the energy of polymerization. Phosphorus may serve as an example:*

$$[P] \rightarrow (P_4) = 18 \text{ kcal./gm. atom (M)}$$
$$(P_4) \rightarrow 2(P_2) = 30 \text{ kcal./gm. atom (M)}$$
$$(P_2) \rightarrow 2(P) = 58 \text{ kcal./gm. atom}$$
$$\overline{[P] \rightarrow (P) = 106 \text{ kcal./gm. atom}}$$

* Here and in table 1 data taken from J. W. Mellor's *Comprehensive Treatise* and from Landolt and Boernstein's tables are marked by (M) and (LB) respectively. (W) and (F) denote estimates by means of Walden and Forcrand's rules respectively. [ ] stands for the solid, ( ) for the gaseous state, no bracket marks the liquid state.

The values used here are 25 kcal./gm. atom for Br, 21 for I, 106 for P, 104 for As, 95 for Sb, 68 for Bi, 59 for S, and 48 for Te; they are not all of equal accuracy, some of them comprising estimated values. For the gaseous elements N_2, Cl_2, O_2 half of the optical energies of dissociation is used. The results are given in table 1.

§ 4. DISSOCIATION PROCESSES AND BOND ENERGIES

In order to correlate the energies of photolytic decomposition, as measured by the continuous absorption spectrum, to particular processes of photodissociation, we have to compare them with the bond energies of the molecules in question. For this purpose we divide the energies of dissociation into constant parts, corresponding to particular bonds. Thus from $\frac{1}{3}D(PCl_3)$ we get the energy of the P—Cl bond as 87 kcal./mol. It should be clearly understood that these values, which we shall call the "*mean bond-energy*" D_B, are not identical with the true energies of the bonds in question. On the contrary, on account of the repulsive forces between the atoms in the formation of this molecule the first Cl atom of PCl_3 is probably linked to P with a greater amount of energy than the second and third Cl, i.e. $D(P+Cl) > D(PCl+Cl) > D(PCl_2+Cl)$. Since the process of photodissociation begins with the completed molecule, the mean bond energies will be upper limits.

It can be seen, however, that an approximate additivity exists, since it is possible to represent, e.g., the energy of dissociation of the oxychlorides as the approximate sum of the mean bond energies derived from the chlorides and oxides. Thus, for example,

$$D(PCl_3) = 261; \quad D_B(P^{III}—Cl) = 87.$$
$$D(PCl_5) = 343; \quad D_B(P^{V}—Cl) = 69.$$
$$D(P_2O_5) = 833; \quad D_B(P^{V}=O) = 167.$$
$$3D_B(P^{V}—Cl) + D_B(P^{V}=O) = 374; \quad D(POCl_3) = 386.$$

Again,
$$D(SbCl_5) = 331; \quad D_B(Sb^{V}—Cl) = 66.$$
$$D(SbCl_3) = 262; \quad D_B(Sb^{III}—Cl) = 87.$$
$$D(Sb_2O_3) = 502; \quad D_B(Sb^{III}=O) = 167.$$
$$D_B(Sb^{III}=O) + D_B(Sb^{III}—Cl) = 254; \quad D(SbOCl) = 260.$$

In organic chemistry an approximate additivity of the mean bond energies has been known for a long time and used in all calculations based on the heats of combustion; in inorganic chemistry, however, this does not appear to have attracted much attention as yet. Considering the uncertainty and inaccuracy of many of the figures used, the agreement between the calculated and observed figures is quite satisfactory. Among the chlorides and oxychlorides of sulphur, similar calculations are possible, but are more difficult because the energy of formation of gaseous SCl_2 is not known. Asundi and Samuel[14] have shown, however, that the bond energies of the derivatives of di- and tetravalent sulphur remain approximately constant, if the results of optical measurements are used.

Table 1

Molecule	Equation		L	S	D	Observed long-wave limit λ (A.)	kcal./mol.	Ref.	Notes
(PBr_3)	$[P]+\frac{3}{2}Br_2=PBr_3$	+ 42·6 (M)	3 (W)		218				
(PCl_3)	$[P]+\frac{3}{2}(Cl_2)=(PCl_3)$	+ 69·7 (LB)			261				
(PBr_5)	$[P]+\frac{5}{2}Br_2=[PBr_5]$	+ 63·5 (M)		11 (F)	280				
(PCl_5)	$[P]+\frac{5}{2}(Cl_2)=[PCl_5]$	+ 107 (LB)		12 (F)	343				
(P_2O_5)	$2[P]+\frac{5}{2}(O_2)=[P_2O_5]$	+ 358 (LB)		30 (F)	833				
($POCl_3$)	$[P]+\frac{1}{2}(O_2)+\frac{3}{2}(Cl_2)=POCl_3$	+ 145 (LB)	9 (LB)		386				
($AsCl_3$)	$[As]+\frac{3}{2}(Cl_2)=AsCl_3$	+ 74·7 (LB)	7 (M)		257				
($SbCl_3$)	$[Sb]+\frac{3}{2}(Cl_2)=[SbCl_3]$	+ 91·4 (LB)		10 (F)	262				
(SbOCl)	$[Sb]+\frac{1}{2}(O_2)+\frac{1}{2}(Cl_2)=[SbOCl]$	+ 89·8 (M)		12 (F)	260				
($BiCl_3$)	$[Bi]+\frac{3}{2}(Cl_2)=[BiCl_3]$	+ 91 (LB)		18 (M)	226				
(PI_3)	$[P]+\frac{3}{2}[I_2]=[PI_3]$	+ 10·9 (LB)		10 (F)	169	3147	90·4	(2)	(*a*)
($AsBr_3$)	$[As]+\frac{3}{2}Br_2=[AsBr_3]$	+ 45·5 (LB)		14 (F)	208	3248	87·6	(2)	(*a*)
(AsI_3)	$[As]+\frac{3}{2}[I_2]=[AsI_3]$	+ 13·5 (LB)		12 (F)	168	5616	50·6	(2)	(*a*)
($SbBr_3$)	$[Sb]+\frac{3}{2}Br_2=[SbBr_3]$	+ 61·4 (LB)		11 (F)	220	5450	52·2	(2)	(*a*)
($SbCl_5$)	$[SbCl_3]+(Cl_2)=SbCl_5$	+ 13·8 (M)		11 (LB)	331	4130	68·9	(2)	(*a*)
(SbI_3)	$[Sb]+\frac{3}{2}[I_2]=[SbI_3]$	+ 28·8		13 (F)	173	4150	68·3	(1)	(*b*)
(N_2O_5)	$(N_2)+\frac{5}{2}(O_2)=(N_2O_5)$	− 1·2			451·8	2800	101	(16)	(*c*)
(Cl_2O)	$(Cl_2)+\frac{1}{2}(O_2)=(Cl_2O)$	− 23			93	6665	45·5	(17)	(*d*)
(SO_3)	$[S]+\frac{3}{2}(O_2)=(SO_3)$	+ 91·9 (LB)			327	3300	86·7	(18)	(*e*)
(TeO_3)	$[Te]+\frac{3}{2}(O_2)=[TeO_3]$	+ 83·6 (M)		*ca.* 24	284	4600	62·1	(16)	

(*a*) Trivedi[2] observed no structure such as is observed by Butkow and ourselves; the vapour pressure was too high. His energy values are therefore too small; the correct values for the vibrationless molecule will probably be 10 to 20 per cent higher.

(*b*) Butkow[1] also investigated BiI_3 and $BiBr_3$, but no thermochemical data are available for these substances.

(*c*) Urey, Dawsey and Rice[15] observed a long-wave limit at λ 3050. Dutta and Sen Gupta[16] observed two regions of absorption, one with a long-wave limit at λ 2800 and another extending from about λ 4500 to λ 3200. This continuum, as may be seen in the published spectra, appears in the middle of the NO_2 band system (also present) and is solely due to NO_2. Any system of absorption bands can be made to appear as a pseudo-continuous spectrum if the vapour pressure, and therefore the population of the higher vibrational levels, is high enough, until for the liquid state only the envelope of the system remains as continuous absorption. As can be seen from a Franck-Condon diagram, the overlapping will always begin in the middle of the system and spread towards longer and shorter wave-lengths. The new bands at shorter wave-lengths are due to transitions from higher vibrational levels of the ground state at small internuclear distances, those at longer wave-lengths to the same transitions at larger internuclear distances. We shall therefore ignore this first absorption and accept as the real absorption of N_2O_5 their value of λ 2800 or 101 kcal./mol., this being slightly the higher value.

(*d*) This long-wave limit is due to the dissociation process $Cl_2O \rightarrow ClO + Cl$; various maxima indicate further processes of photodissociation into unexcited and excited products.

(*e*) The first absorption maximum observed by Dutta[18] has a long-wave limit at λ 3300. The second absorption region is correlated to the process $SO_3 \rightarrow SO_2 + O(^1D)$. The absorption spectra of SCl_2, $SOCl_2$, S_2Cl_2, and SO_2Cl_2 have recently been measured by Asundi and Samuel[14]. For the calculation of the atomic heat of formation a rough value of 90 kcal./mol. was used for $D(S_2)$, instead of 88. With this correction the energies of dissociation are: $D(SCl_2) = 125$, $D(SOCl_2) = 214$, $D(S_2Cl_2) = 181$, and $D(SO_2Cl_2) = 316$. The value of $D(SCl_2)$, however, refers to sulphur dichloride dissolved in sulphur monochloride, the correct value therefore will be smaller. For the homologous molecule Cl_2O the heat of solution in water is 9·4 (LB). Since the dipole moments are certainly smaller in our case, we may take $D(SCl_2)$ as approximately 120. The long-wave limits are: SCl_2 λ 4162 or 68·4 kcal./mol. ($SCl_2 \rightarrow SCl + Cl$) and λ 4770 or 104 kcal./mol. ($SCl_2 \rightarrow S + 2Cl$); $SOCl_2$ λ 2900 or 97 kcal./mol. ($SOCl_2 \rightarrow SO + 2Cl$);

The above figures show that the rule of additivity obtains only so long as the central atom does not change its state of valency. It is, for instance, not possible to represent the dissociation energy of $POCl_3$ if the value of $D_B(P^{III}—Cl)$ is employed, or that of SbOCl by means of $D_B(Sb^{V}—Cl)$. Furthermore, the mean bond energy of a lower state of valency is always bigger than that of a higher one. The bond energies of di- and tetravalent sulphur derivatives remain, however, apparently constant. This clearly indicates that the difference of the mean bond energies is produced by the activation of the helium-like repulsive group of electrons, which remains an s^2 group with respect to the central atom in PCl_3, SCl_2, $SOCl_2$, and therefore must have undergone fission, i.e. must have been transferred to an *sp* or p^2 group, in $POCl_3$, SO_2Cl_2, etc., causing a rearrangement of the electronic configuration of the molecule. Exactly the same behaviour is well known from molecular refractivity and parachor[19]. This is not astonishing, since any molecular quantity which follows approximately the law of additivity may be subdivided in two different ways: either by introducing additive constants for the various atoms or for the various bonds. But each kind of division will always retain some of the features of the other kind.

Besides the mean bond energies there exists, however, a second set of figures, which we have to take into account for the sake of comparison. For derivatives of penta- and hexavalent atoms the energies of certain dissociation processes are independently known, either by direct measurements or as the difference of two atomic heats of formation. Thus, by adding $\frac{1}{2}D(O_2)=58{\cdot}7$ to the equation

$$(SO_2)+\tfrac{1}{2}(O_2)=(SO_3)+23{\cdot}5,$$

we obtain about 82 kcal./mol. for the process of dissociation $(SO)_3 \rightarrow (SO_2)+(O)$; if we add $D(SO_2)=247$ to this, we obtain $D(SO_3)=329$ kcal./mol., whereas calculation from the elements gives 327 kcal./mol. Such values, directly determined by thermochemical experiments, we shall denote by D_T. They are, of course, entirely different from bond energies, which measure the *adiabatic* dissociation of a molecule. Thus the diamagnetic molecule SO_3 is certainly not formed by the chemical union of unexcited SO_2 and unexcited O atoms. The ground level of O is the paramagnetic ^3P term, whereas SO_2 possesses a diamagnetic ground level and their combination does not allow for a diamagnetic ground level of SO_3. Of the products of adiabatic dissociation of SO_3 into SO_2+O, therefore, at least one is excited, i.e. in an energy diagram, the curve of *adiabatic* dissociation connects the ground state with the level of excited atoms or radicals. D_T, on the other hand, measures the difference of the energy contents of the two systems SO_3 and SO_2+O with respect to the level of the unexcited dissociation products, without regard to the actual adiabatic formation of the molecule. Since all the saturated molecules dealt with here are diamagnetic, and all the atoms in question belong either to the sixth or to the seventh group with paramagnetic ground states, the same is true of all of them. Also, in cases like the dissociation $PCl_5 \rightarrow PCl_3+2Cl$, it is established by the magnetic properties of the molecules and atoms, that at least one of the products of the adiabatic dissociation is excited.

Table 2

Molecule	Dissociation process	Mean bond energy D_B	Thermo-chemical energy D_T	Optical dissociation energy D_O	$D_O - D_T$	$D_O - D_B$	Reference
N_2O_5	$O_2N—O—NO+O$	90·2	—	101	—	11	(15)
	$2NO_2+O$	—	63·8	101	37	—	(16)
PCl_3	PCl_2+Cl	87	—	101	14	—	Present paper and (2)
PBr_3	PBr_2+Br	73	—	92	19	—	Present paper
PI_3	PI_2+I	56	—	87	31	—	(2)
PCl_5	PCl_4+Cl	69	—	108	39	—	Present paper
	or PCl_3+2Cl	—	75	108	—	33	
PBr_5	PBr_3+Br	58	—	90	32	—	,, ,,
	or PBr_2+2Br	—	60	90	—	30	
$POCl_3$	$POCl_2+Cl$	69	—	127	58	—	,, ,,
	or PCl_3+O	—	125	127	—	2	
P_2O_5	P_2O_4+O	167	—	129	−38	—	,, ,,
	or $\frac{1}{2}P_2O_3+O$	—	?	129	—	?	
$AsCl_3$	$AsCl_2+Cl$	86	—	106	20	—	Present paper and (2)
$AsBr_3$	$AsBr_2+Br$	69	—	>88	>19	—	(2)
AsI_3	AsI_2+I	56	—	>51	>−5	—	(2)
$SbCl_3$	$SbCl_2+Cl$	87	—	99	12	—	Present paper and (2)
$SbBr_3$	$SbBr_2+Br$	73	—	>52	>−21	—	(2)
SbI_3	SbI_2+I	57	—	68	10	—	(1)
$SbOCl$	$SbO+Cl$	87	—	117	30	—	Present paper
$SbCl_5$	$SbCl_4+Cl$	66	—	>69	>3	—	(2)
	or $SbCl_3+2Cl$	—	81	>69	>−12	—	
$BiCl_3$	$BiCl_2+Cl$	75	—	85	10	—	Present paper and (2)
Cl_2O	$ClO+Cl$	46·5	43	43	0	−3·5	(17)
SCl_2	$SCl+Cl$	<60	—	55	<5	<5	(14)
SCl_2	$S+2Cl$	<120	—	104	>−16	—	(14)
$SOCl_2$	$SO+2Cl$	96	—	97	1	—	(14)
S_2Cl_2	S_2+2Cl	93	—	104	11	—	(14)
SO_2Cl_2	$SOCl_2+O$	—	102	109	—	7	(14)
SO_3	SO_2+O	109	82	87	−22	5	(18)
TeO_3	TeO_2+O	95	53	62	−33	1	(16)

In this connexion it is of interest to note, that the values D_T are always smaller than the corresponding values of D_B. This clearly indicates that the adiabatic dissociation does indeed reach a higher level of the separated system. It seems likely that this is connected with the conception of the s^2 group undergoing fissure in order to lose its repulsive character, since this again involves the excitation of one of the dissociation products.

In table 2 the long-wave limits D_O of the absorption spectra are compared with the values of D_B and D_T, and it appears as if several general rules can be derived therefrom. We consider first the molecules formed by the trivalent atoms of the fifth group. Here D_O is always much bigger than D_B. The true bond energy of the halogen split off first will even be less than D_B, and we have therefore to assume that the long-wave limit represents a transition from the ground state of the molecule to a very steep repulsive curve. The width of the first absorption region also points in this direction. Since all these molecules exhibit a covalent linkage, as indicated by their conductivity, low boiling point, dipole moment and Raman effect, Butkow[1] assumes that the products of the first photolytic dissociation are an unexcited radical and an excited halogen atom. This assumption, which is based on Franck's criterion of the ionic or electrovalent linkage[7], cannot be proved directly, since the exact energy of dissociation is not known.

It has been shown, however, that it is not possible to ascribe general validity to Franck's criterion, although it holds good in many simple di- and triatomic molecules. As Herzberg and Franck and his collaborators have shown[21], it cannot be rigorously valid, because intersections of the potential curves of covalent molecules occur, and therefore Franck's criterion is a necessary but insufficient condition of electrovalent linkage. Thus the ground level of a covalent molecule may be formed by the combination of excited atoms; consequently an excited level of the molecule may involve unexcited products of dissociation; such a case probably occurs in the absorption spectra of the oxides of the second group[20]. Further, if the number of valencies and atoms is increased, it becomes more and more probable that a repulsive curve originates in the level of the unexcited separated atoms besides the attractive curve of the ground state (this case may be considered as the same, i.e. as an intersection at large internuclear distances). Considering the figures of table 2, we expect the difference $D_O - D_B$ to increase from Cl to Br to I, since the respective energies of excitation ($^2P_{\frac{1}{2}}$–$^2P_{\frac{3}{2}}$) are 2, 8·7 and 21·6 kcal./mol. This is indeed indicated in the series PCl_3, PBr_3, and PI_3. The heavier molecules, however, do not follow this rule; and the absolute figures, say of SbI_3, do not permit one to deduct 21·6 kcal./mol. from the value of D_O; unless it becomes possible to reduce the thermochemical figures as a result of new measurements, it seems probable that this steep repulsive curve originates in the level of the unexcited dissociation products. This is also indicated by PBr_3, where the second region of absorption seems to represent the dissociation into PBr_2 and excited Br. Furthermore the steepness of the repulsive curve, which is evident from the width of the absorption region, also indicates that it will run down to the level of the unexcited atoms. SbOCl behaves like other molecules of this series, and the mean bond energies

indicate that it is the Cl atom which is removed first, the mean energy of the $Sb^{III}{=}O$ bond being too large.

As to the molecules formed by the pentavalent atoms of the fifth group, it can be seen that the D_O values agree better with the D_T than with the D_B values. This is not so apparent for cases where the D_T values refer to the dissociation of two halogen atoms, but the agreement is very good indeed where a single O atom is split off, as in SO_2Cl_2, SO_3, and TeO_3. In all these cases the first region of selective absorption represents the transition from the ground state to a flat repulsive curve, which originates in the ground level of that molecule in which the valency state of the central atom is diminished by 2. The products of dissociation are unexcited atoms and molecules. The less satisfactory agreement in cases where two halogen atoms are removed simultaneously finds its explanation, if we consider that the energy diagram of such a process can hardly be approximated any longer by a two-dimensional Franck-Condon diagram. Not much is known at present about such conditions, but it seems probable that the repulsive plane in question may be deformed by the presence of the second halogen atom. For N_2O_5 the case is slightly different. We are able to calculate thermochemically the energy of the dissociation process $N_2O_5 \rightarrow N_2O_4 + O$ or $N_2O_5 \rightarrow 2NO_2 + O$. But N_2O_4 is formed by polymerization of two NO_2 molecules, $O_2N{-}NO_2$, whereas N_2O_5, the normal derivative of pentavalent nitrogen, has the formula $O_2N{-}O{-}NO_2$. Since it is improbable that the middle O atom will be split off, the remaining N_2O_4 radical will possess the formula $O_2N{-}O{-}NO$, as distinct from the N_2O_4 molecule. In this case therefore D_B approaches nearer to D_O than to D_T, which in reality belongs to a different molecule.

As to the molecules of the di- and tetravalent atoms of the sixth group the agreement of the energy value of the long-wave limit with thermochemical and band-spectroscopic data has already been commented upon. The photodissociation of these molecules clearly indicates that the bond energies remain almost unchanged in the transition from diatomic to polyatomic molecules[14]. This seems to be connected with the fact that the elements of the sixth group form diatomic molecules, which, according to the pair-bond interpretation of the method of molecular orbitals, already possess two free valencies.

§ 5. CONCLUSIONS

Even a preliminary theoretical interpretation of the behaviour of such higher polyatomic molecules in the process of photolytic dissociation has to pay regard to the following points: (1) Molecules formed by atoms of the fifth and sixth group in their maximal state of valency dissociate in such a way that the dissociation products are unexcited atoms and an unexcited saturated molecule formed by the central atom in its next lower state of valency. (2) The thermochemical energies of these dissociation processes are considerably smaller than the corresponding mean bond energies. (3) The magnetic properties of these molecules show that at least one of the products of *adiabatic* dissociation is excited. (4) Molecules formed by

trivalent P, etc., and by di- and tetravalent S dissociate into atoms and radicals which are probably also unexcited. The repulsive curve is steep in the case of derivatives of trivalent P and similar molecules and rather flat for molecules formed by di- and tetravalent S. (5) The mean bond energies are always smaller than the energy value of the long-wave limit.

Considerations (1), (2), and (3) together indicate clearly that the flat repulsive curve which produces the photodissociation of these molecules of higher valency is intersected by the curve of the adiabatic dissociation. The same curve of adiabatic dissociation of the molecules of lower valency state in their ground state, however, involves unexcited radicals and atoms. This is schematically shown in figures 6 and 7, which represent the energy levels of PBr_3 and SO_3 and their constituent atoms. The diagram (figure 6) for PBr_3 is simple and exactly as expected; from the level of the separated system $PBr_2 + Br$ two curves originate, one attractive which

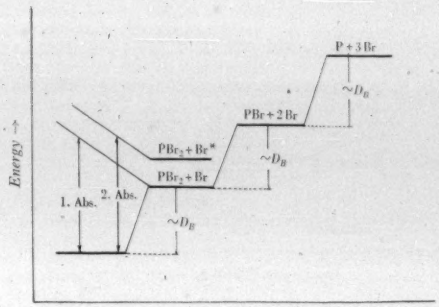

Figure 6.

ultimately forms the ground level of PBr_3, and one repulsive which is the final state for the first region of selective absorption; the second region suggests a second repulsive curve, involving an excited Br atom. This is not so in figure 7, where the ground level of SO_3 does not form part of the same system of ground states as that of SO_2. The second region of absorption is correlated to the process $SO_3 \rightarrow SO_2 + O(^1D)$, and this indicates that the ground state of SO_3 involves an excited SO_2 molecule. The true bond energy of SO_3 cannot therefore be compared either to D_T or to $D_E(SO_3) = \frac{1}{3}D(SO_3)$, since the adiabatic dissociation certainly does not lead to four unexcited atoms. This view, which alone appears to be able to cover all the four points mentioned above, was stated earlier for the explanation of such phenomena[3]. It was then suggested that the fact, which is now rather certain, that no attractive curve originates in the level of unexcited $SO_2 + O(^3P)$ or $O(^1D)$, may be connected with the repulsive character of the s^2 group, the "lone pair" of S, which has to become active during the formation of SO_3. This, of course, cannot be proved by the present experiments. We can only say that at least one of the four separated

atoms S+3O involved in the adiabatic formation or dissociation of SO_3, will be excited, but we do not know which atom it is and in which way the excitation takes place. But this hypothesis seems to be quite probable, since the repulsive character of the s^2 group is theoretically clear beyond doubt, and has been experimentally confirmed by the band spectra of molecules formed by atoms of the second group, and also by the extremely high energy of adiabatic dissociation of CO_2[22]. Apparently CO_2 is not a single case, but according to the continuous absorption spectra we may expect all molecules to behave similarly, if formed by atoms of the higher groups in their maximal state of valency.

The difference in steepness of the repulsive curves for the different types of molecules remains to be explained; the slope obviously depends on various factors and a full interpretation is not yet possible. But we may say that in a case like PCl_3, where both the ground state and the repulsive curve originate in the same level,

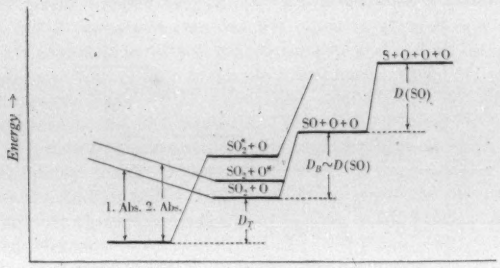

Figure 7.

probably of an unexcited atom and an unexcited radical, a steep repulsive curve may be expected. This case is similar to that of the formation of H_2; here Heitler and London's calculation[23] has shown, that on account of the removal of the degeneracy the original energy value of the degenerated system H+H is replaced by two new energy levels, one lower and one higher than the original common one. On decreasing internuclear distance these two levels form the ground state and a repulsive state respectively, and the slope of the potential curve of the latter will be very steep indeed on account of wave-mechanical repulsion. The absorption spectra of molecules like CH_3Cl are also of interest in this connexion[4], since they show the same type of steep repulsive curves, and conditions are somewhat clearer in such a case, because the CH_3 radical will better approximate a "united atom". We may term these two the "bonding" and the "anti-bonding" curves more or less in accordance with the Herzberg-Mulliken terminology. From the level of the system SO_2+O, however, only one curve originates, which is not split into two and may be considered neither as bonding nor as anti-bonding but as non-bonding. Here the Van der Waals forces predominate, rendering the curve flat. But such a view does not yet explain the small slope of the curve in molecules like $SOCl_2$ nor the steepness

of it in molecules like PCl_5. As pointed out above, we believe at present that the former case is connected with the existence of free valencies in the molecule SO, the latter with the greater complexity of a multi-dimensional Franck-Condon model.

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SOME EXPERIMENTS WITH NEUTRONS HAVING THERMAL ENERGIES

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ABSTRACT. Moon and Tillman have found a large influence of temperature upon the properties of neutrons within a cavity in a block of paraffin wax; on the other hand, Dunning, Pegram, Fink and Mitchell, using a lithium-lined ionization chamber, found no detectable influence of temperature upon the number of disintegrations of lithium produced by neutrons leaving the surface of a can of water which contained a radon-beryllium source of fast neutrons.

This apparent discrepancy has been investigated; the various explanations hitherto proposed have been found inadequate, and the difficulty has been resolved by an experimental proof that the activity produced in a specimen of silver when it is exposed within a thin-walled wax cylinder to the neutrons emerging from a large block of wax shows nearly as great a dependence upon the temperature of the cylinder as when the system is exposed within a cavity in the large block. The failure to find effects of temperature with the emergent neutrons was therefore due not to an absence of neutrons having thermal velocities but to an ineffective means of changing the temperature of these neutrons.

§ 1. INTRODUCTION

The neutrons produced in the nuclear reaction ${}^{9}_{4}\mathrm{Be}+{}^{4}_{2}\mathrm{He}={}^{12}_{6}\mathrm{C}+{}^{1}_{0}n$, when allowed to diffuse through paraffin wax, may have their velocities reduced to such an extent by collisions with the hydrogen nuclei present that they are able to attain some measure of thermal equilibrium with the wax. This fact was established in the following way[1]. A radon-beryllium source of neutrons was placed in a large block of wax some 10 cm. from a cavity whose walls, to a depth of about 1 cm., could be kept either at room-temperature or at the boiling-point of liquid oxygen. A Geiger counter was used to measure the β-ray activity induced in a thin specimen of silver which had been exposed for a known time in the cavity. When the temperature of the walls was 90° K. the activity obtained was considerably greater than when they were at room-temperature. Two conclusions are to be drawn from this experiment. Firstly, many of the neutrons crossing the cavity and responsible for the activity induced in the specimen must have energies of the order of those of thermal agitation (0·03 volt). Secondly, the cross-section of the silver nucleus for capture of a neutron must increase with decreasing velocity of collision. Measurements showed that the nuclei of rhodium, copper, iodine, dysprosium, and other elements behave, qualitatively at least, in a manner similar to that of the silver nucleus. It was typical of these experiments that the specimens were always

irradiated inside cavities in the paraffin wax. If the thickness of the cooled wax was greater than 1 cm. the effect of its change of temperature was less, owing to increased absorption by the cold wax: with very thick layers (4 cm. or more) the effect of temperature was zero or even reversed.

Dunning, Pegram, Fink and Mitchell[2], who were also searching for evidence of the existence of thermal neutrons, used a different geometrical arrangement. The source of fast neutrons was placed inside a large can of water, but the detector of the slow neutrons, a lithium chamber, was at some distance away outside. The whole of the water could be cooled from 373° to 90° K. The number of disintegrations of lithium nuclei per minute showed no definite increase with the cooling of the water. The absorption by a thin sheet of cadmium of the neutrons emerging from the water was measured also: a very small increase in the absorption coefficient of this element was noted when the temperature of the water was lowered. In order to meet the objection involved in the use of thick layers of cooled material, these authors[3] later made further measurements with lithium detection and cadmium absorption, cooling thin layers instead of thick. No significant differences were observed.

Four explanations of their results are possible. (1*a*) Lithium may not detect neutrons having thermal velocities; (1*b*) the detection of neutrons by lithium and their absorption by cadmium, though extending to thermal velocities, may be insensitive to change of velocities; (2*a*) not many of the neutrons coming from the water may have thermal velocities; (2*b*) thermal neutrons, though present, may not change their temperature appreciably in passing through a thin slab of cold wax. Of these possible explanations (1*a*), (1*b*) and (2*a*) have been pointed out by Dunning.

The experiments to be described in this paper may be summarized as follows. (i) Dunning's experiment was repeated with detectors of silver and of boron, for which explanations (1*a*) and (1*b*) were already known to be untenable. (ii) Explanations (1*a*) and (1*b*) were tested for the cases of lithium and cadmium by measurements of the absorption by these elements of neutrons whose velocities were known to be thermal. (iii) Explanations (1*a*) and (1*b*) having now been dismissed, calculations were made[7] which showed (2*a*) to be improbable. Explanation (2*b*) was therefore investigated and was found to agree with experiment.

The experiments will now be described in detail.

§ 2. MEASUREMENTS MADE OUTSIDE A BLOCK OF WAX

For the first experiments a thin specimen of silver was used as a detector of slow neutrons. The apparatus is shown in figure 1. A radon-beryllium source of neutrons was placed at the centre *C* of a fairly large block of wax *W*, and one or other of two thin slabs of wax, identical in all respects but temperature, was interposed between *W* and *S* at *D*. One slab was kept at room-temperature, 290° K., and the other at the boiling-point of liquid oxygen, 90° K.

The specimen of silver was placed at *S* and exposed to the beam of slow neutrons

for 1 min. with the slab at D at room-temperature. A measure of the β-ray activity induced in the specimen was obtained in the usual way with a Geiger counter, amplifier, and mechanical counter. When the cold slab was substituted the activity was greater in the ratio 1·06 : 1. The probable error was $\pm 0{\cdot}04$, so that the increase is scarcely definite.

A boron-lined ionization chamber was next placed at B and used as a detector of slow neutrons. It was connected to a linear amplifier and mechanical counter. Runs having a duration of 1 min. were made, the warm and cold slabs being placed

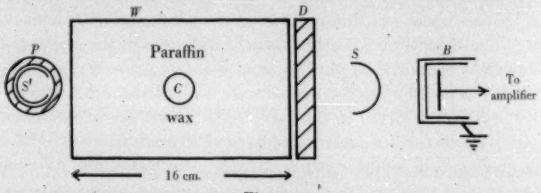

Figure 1.

at D in turn. Although the number of α particles recorded in all was well over 10,000, the rate of counting with the cold slab at D was no greater than with the warm slab. The final ratio was

$$\frac{\text{count with cold slab}}{\text{count with warm slab}} = 1{\cdot}01 \pm 0{\cdot}03.$$

Thus a change in the temperature of the outer layers of the paraffin wax has little influence upon the numbers of neutrons recorded by silver and boron detectors. Since[1] silver and boron respond to thermal neutrons and are sensitive to change in their velocity, explanations (1 *a*) and (1 *b*) cannot hold for these elements, though they still might hold for the lithium detector used by Dunning.

§ 3. ABSORPTION MEASUREMENTS

In order to see whether explanations (1 *a*) or (1 *b*) may yet hold for lithium and cadmium, an apparatus similar to that used by Moon and Tillman in their original experiments on temperature effects was set up, figure 2. The hollow cylinder of wax P inside the Dewar vessel D had a wall-thickness of 1 cm. The source of neutrons C was about 8 cm. from D. A thin specimen of silver was irradiated at S with the cylinder at room-temperature and the β-ray activity was measured. A lithium absorber in the form of a cylinder was then placed at A, around S. The activity induced in the silver was again measured, after irradiation at S with A in position. These two measurements were repeated with P at 90° K. The transmission factors were calculated in each case.

Boron and cadmium absorbers also were investigated. The results are given in table 1. Use was made of the two periods of silver, 22 sec. and 2·5 min. For the

measurements with the shorter period the lithium absorber contained 0·3 g./cm.^{2}, while for the longer period it contained 0·2 g./cm.^{2} The boron absorber contained 0·03 g./cm.^{2} and the cadmium 0·015 g./cm.^{2} If, for the sake of comparing the behaviour of the three elements, we assume the absorption in all cases to follow an exponential law we can obtain λt for any of the elements used, where λ is the absorption coefficient (cm.^{2}/g.) and t is the mass of the absorber (g./cm.^{2}). If λ_1 refers to room-temperature neutrons and λ_2 to 90°-K. neutrons, λ_2/λ_1 is calculable. This ratio has been included in the table.

λ, t

λ_1

λ_2

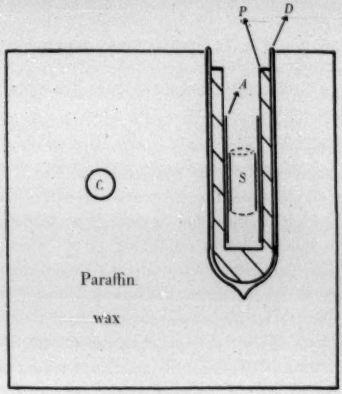

Figure 2.

Table 1

Absorber	Detector	Silver, 22 sec. period	Silver, 2·5 min. period
Lithium	290° K.	$0{\cdot}38_8 \pm 0{\cdot}01_6$	$0{\cdot}51_0 \pm 0{\cdot}01_7$
	90° K.	$0{\cdot}30_3 \pm 0{\cdot}01_5$	$0{\cdot}41_0 \pm 0{\cdot}01_8$
	λ_2/λ_1	$1{\cdot}27 \pm 0{\cdot}07$	$1{\cdot}32 \pm 0{\cdot}06$
Boron	290° K.	$0{\cdot}44_5 \pm 0{\cdot}02$	$0{\cdot}39_8 \pm 0{\cdot}02$
	90° K.	$0{\cdot}37_4 \pm 0{\cdot}02$	$0{\cdot}32_8 \pm 0{\cdot}01_5$
	λ_2/λ_1	$1{\cdot}21 \pm 0{\cdot}08$	$1{\cdot}21 \pm 0{\cdot}07$
Cadmium	290° K.	—	$0{\cdot}50_5 \pm 0{\cdot}01_5$
	90° K.	—	$0{\cdot}43_0 \pm 0{\cdot}01_5$
	λ_2/λ_1	—	$1{\cdot}24 \pm 0{\cdot}06$

The ratio of the activity induced in the specimen with P at 90° K. to that induced with P at 290° K., with no absorber present, was $1{\cdot}27 \pm 0{\cdot}04$ for the shorter period of silver and $1{\cdot}35 \pm 0{\cdot}04$ for the longer. These figures are in agreement with the previous results[1].

The table tells us at once that the absorption of slow neutrons by lithium and cadmium is appreciable for very low velocities of the neutron, and is sensitive to changes of these velocities. Explanations (1*a*) and (1*b*) cannot be true, therefore, for any of the elements silver, boron, lithium and cadmium.

Now explanation (2*a*) is improbable for two reasons. The experiments of Dunning[4] and others with a velocity-selector show directly the presence of some neutrons having thermal energies amongst those emerging from a face of a block of wax. Moreover, Moon's calculations[7] indicate that quite a fair proportion of the activity induced in a silver specimen exposed outside a block of wax should be due to thermal neutrons.

§ 4. THE PROPOSED EXPLANATION

We are left with the last possibility, (2*b*). It was realized that the inside and outside experiments differed in that in the former case the specimen was completely surrounded by the wax layer. At the suggestion of Dr P. B. Moon I tried the following experiment. A source of fast neutrons was placed at the centre of a large block of wax W and a hollow cylinder of wax P of wall-thickness 0·6 cm. just outside, figure 1. The specimen was irradiated at S'. The activity induced in a silver specimen was increased by a factor of $1{\cdot}28 \pm 0{\cdot}07$ when the cylinder P was cooled from 290 to 90° K. A separate experiment showed that very little of the activity induced was due to fast neutrons scattered in P.

We conclude that many of the neutrons reaching P from W have energies as low as those of thermal agitation. It is from the results obtained with a cylinder of wax and not from those with a block of wax that we are able to draw this conclusion. A thermal neutron leaving W and entering P may cross and recross the hollow of the cylinder many times before being captured by the specimen at S'. Its chance of reaching thermal equilibrium with P is high. Had P been used inside a cavity, such as that occupied by the Dewar vessel in figure 2, measurements with a silver detector having a period of 22 sec. would have given an increase of activity of about 1·33. Whether the value of $1{\cdot}28 \pm 0{\cdot}07$ is definitely less than that to be obtained with P inside is a question of some importance, but a more accurate determination of this value (e.g. to within $\pm 0{\cdot}02$) would involve the counting of a very large number of particles.

§ 5. DISCUSSION OF RESULTS

The neutrons that are highly absorbed by silver, called Group A by Fermi[5], are more prominent outside a block of wax than inside: they are believed to have energies above those of thermal agitation. Again, when silver is exposed inside a cavity in a block of wax, the induced activity can be reduced to about one-eighth its original value by surrounding the specimen with a thick (0·5 mm.) sheet of cadmium: if, on the other hand, the silver be exposed outside a block of wax, the sheet of cadmium when interposed between wax and silver reduces the activity only to 45 per cent of its original value. These two experimental results suggest that

thermal neutrons are present in rather smaller proportions outside than inside a block of wax. Moon's calculations support this suggestion.

Lithium, cadmium, and boron have all shown increased absorption of slow neutrons with decreasing velocity of the neutron. Boron has already been mentioned[1]. Westcott and Niewodniczański[6], making measurements similar to those described here, have reported a value of $1{\cdot}07 \pm 0{\cdot}04$ for λ_2/λ_1 in cadmium. They stated that their absorber was rather thick, 0·039 g./cm^2; the discrepancy between their value and that obtained here, $1{\cdot}24 \pm 0{\cdot}06$, is mainly due to the assumption of an exponential absorption. The thicker the absorber, the less accurate is this assumption.

Much of the recent work on the properties of slow neutrons has been done with the beam of neutrons emerging from a block of wax. It was important that we should have some knowledge of the energy-distribution in such a beam. Some of the experiments had pointed to the presence of thermal neutrons in the beam, but Dunning's temperature experiment had remained outstanding. It was the main purpose of the present work to inquire into the apparent discrepancy between that temperature experiment and those of Moon and Tillman. That discrepancy has now been removed.

§ 6. ACKNOWLEDGMENTS

The radon was kindly given by the Radiology Committee of the Medical Research Council: I am grateful to Prof. S. Russ for arranging the supplies. I should like also to thank Dr C. E. Wynn-Williams for the loan of the linear amplifier and mechanical counter mentioned in § 2.

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ON THE PASSAGE OF NEUTRONS THROUGH PARAFFIN WAX

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ABSTRACT. The velocity-distribution of neutrons passing through paraffin wax is investigated on the assumption that the collisions made before thermal velocity has been reached are elastic collisions with protons. Within the body of the wax, and provided the variation of free path with velocity is not rapid in the neighbourhood of thermal velocities, thermal neutrons outnumber all others in the ratio of about P to 1, where P is the average number of collisions made by a thermal neutron before it is absorbed. According to Bjerge and Westcott, P is of the order of 80. The number of neutrons crossing unit area is estimated; in this case also the majority have thermal velocities. The velocity-distribution of neutrons emerging from the surface differs from that in the interior, thermal neutrons, though probably still in the majority, being less prominent under the former conditions. The ratio of the flux of thermal neutrons in the interior to that at the surface is calculated and shows satisfactory agreement with the experimental value of about 13 to 1 obtained when the neutrons are estimated from the artificial radioactivity of silver.

§ 1. INTRODUCTION

The purpose of this communication is to gather together some calculations regarding the equilibrium of neutrons with a hydrogen-containing medium. Since water and paraffin wax are widely used for reducing the velocities of fast neutrons, attention will be concentrated upon these two substances, which in this connexion have properties so similar[1] that they will be treated as identical. The experimental facts upon which numerical calculations will have to be based, and those which the calculations will be used to interpret, are not yet known with any great accuracy; there is consequently neither the possibility nor the need for anything more than an estimate of the orders of magnitude concerned. The main object of the calculations is to obtain some idea of the numbers of neutrons of different velocities which are to be expected in the flux of neutrons passing through, or emerging from, a large block of wax irradiated uniformly by very fast neutrons such as those which may be obtained by bombarding beryllium with α particles.

When a uniform supply of fast neutrons is introduced into an infinite bulk of matter, there is set up an equilibrium distribution of velocities, determined by the condition that the number of neutrons entering any velocity group as a result of scattering shall be equal to the number leaving that group as a result either of scattering or of absorption. The scattering of neutrons in wax is due mainly to the hydrogen nuclei; absorption, whether due to hydrogen or to carbon, is believed to

be so small that a neutron having initially a kinetic energy of a million electron-volts or more has a high probability of reaching thermal velocity before being captured. About eighteen collisions with particles of the same mass will on the average reduce the energy of a two-million-volt neutron to the 0·03 volt characteristic of thermal agitation at ordinary temperature; Bjerge and Westcott[1] estimate from their experiments that about eighty collisions are made by the average slow neutron before it is captured.

We may therefore hope to make an approximate calculation of the equilibrium velocity-distribution within a large bulk of wax on the following assumptions: (i) That the collisions made before thermal velocity has been reached are elastic collisions with protons which may be regarded as stationary. The colliding particles will be treated as elastic spheres of equal mass.* (ii) That eighty further collisions, on the average, are made after thermal velocity has been reached.

The velocity-distribution of the thermal neutrons will be very nearly Maxwellian, so in order to describe them completely we need specify only their total number. A more or less arbitrary upper limit C must be set to the velocities which are to be regarded as thermal; this will be taken at twice the average thermal velocity $\bar{c}$. At room-temperature, C will correspond to an energy of about 0·13 V.; a two-million-volt neutron will have to make about sixteen collisions with stationary protons in order to reach such an energy. In default of a suitable positive expression to include neutrons of all energies from 0·13 V. upwards, such neutrons will be called "non-thermal". This arbitrary division will lead to some error in the estimate of the velocity-distribution in the neighbourhood of the velocity C. Velocities of that order seem likely to be of considerable interest[2] and would deserve special investigation, but since the present discussion is concerned only with the broad outline of the velocity-distribution it would be unprofitable to deal with the matter here.

C

$\bar{c}$

§ 2. VELOCITY-DISTRIBUTION FOR NON-THERMAL NEUTRONS IN THE INTERIOR OF A LARGE BLOCK OF WAX

Let S neutrons of velocity U be introduced every second into every unit volume of an infinite bulk of wax; let the mean free path for a neutron of velocity u be $\lambda(u)$, and until a neutron has reached the velocity C (where $C \ll U$) let the laws of collision be as for the elastic impact of a moving sphere upon a stationary sphere of equal mass. The chance that in such a collision a neutron whose velocity was previously v shall acquire a velocity lying between u and $u+du$ is easily shown to be $(2u/v^2)\,du$. If $N(v)\,dv$ be the number of neutrons per unit volume having velocities between v and $v+dv$, the number of collisions made by neutrons of this class is

S, U

u, λ

v

N

$$\frac{v}{\lambda(v)} . N(v)\,dv$$

* The neutron is heavier than the proton by about one part in a thousand. This will make very little difference to the present calculations, but it will mean that a neutron cannot reach thermal velocity in a single elastic collision, because even if the collision is precisely head-on the neutron will retain a four-thousandth part of its original energy.

per cm.^{2} per second, and the number of neutrons thereby transferred to class u is

$$\frac{v}{\lambda(v)} . N(v)\, dv \frac{2u}{v^2}\, du.$$

The total rate of gain of class u is therefore

$$\int_{v=u}^{v=U} \frac{N(v)}{\lambda(v)} . \frac{2u}{v}\, du\, dv$$

per cm.^{2} per sec. Since absorption of the neutrons is being neglected, the rate of loss of class u is equal to the number of elastic collisions made in a second by neutrons of this class, viz.,

$$\frac{u}{\lambda(u)} . N(u)\, du.$$

The velocity-distribution of the neutrons, within the limits $U > u > C$, must therefore satisfy the equation

$$\int_{v=u}^{v=U} \frac{N(v)}{\lambda(v)} . \frac{2u}{v}\, du\, dv = \frac{u}{\lambda(u)} N(u)\, du.$$

This equation is to be solved subject to the condition that the number of neutrons passing through any velocity group in unit time shall be equal to the number S which are introduced at the upper end of the velocity spectrum. It may be verified that when $u \ll U$ (that is, after the first few collisions) the requirements are satisfied by the velocity-distribution

$$N(u)\, du = \frac{2S\lambda(u)}{u^2}\, du^* \qquad \ldots\ldots(1).$$

Since u^2 appears in the denominator, there is a preponderance of the slower non-thermal neutrons whose velocities are not very much above the minimum velocity C to which these calculations apply. If, in and just above the thermal range of velocities, λ does not vary rapidly with u, the total number Q_N of non-thermal neutrons will not be far from that given by

Q_N

$$Q_N = \int_C^U \frac{2S\lambda_0}{u^2}\, du = \frac{2S\lambda_0}{C}, \text{ since } U \gg C \qquad \ldots\ldots(2),$$

where λ_0 is the free path for neutrons of thermal velocity.

λ_0

The number of neutrons of class u crossing a square centimetre (from both sides) in a second is

$$\frac{u}{2} . N(u)\, du = \frac{S\lambda(u)}{u}\, du.$$

The preponderance of the lower velocities is here less marked, and it is less justifiable to take λ as constant and equal to λ_0; however, since λ is of the order of a few millimetres at thermal velocities and rises only to a few centimetres for fast

* Amaldi and others[3] have given the equation

$$N(u)\, du = \text{const.} \times \frac{u\, du}{(u + \lambda/T)^3}$$

for the case where λ is constant but absorption occurs, the absorption law being such that a neutron has a mean life T which is independent of u.

neutrons whose velocities are 10^4 times as great, the assumption of a constant free path of the thermal value is not likely to lead to an entirely wrong order of magnitude. The flux M_N of non-thermal neutrons across unit area is then given by the equation M_N

$$M_N = \int_C^U \frac{S\lambda_0}{u} . du = S\lambda_0 \log_e \frac{U}{C} \qquad \text{.....(3).}$$

In order to form some estimate of the effect of a variable free path, one need only realize that if the free path for any range of velocities be increased n times each neutron stays n times as long within those limits of velocity, and the number of such neutrons is simply increased n times, other velocities being quite unaffected. As an approximation to the (unknown) law of variation of free path with velocity, let us make the rather extreme assumption that λ is equal to five times λ_0 at all velocities above C, the drop to the thermal value at this velocity being sudden. Then instead of equation (2) we shall simply have

$$Q'_N = \frac{10 S\lambda_0}{C} \qquad \text{.....(4).} \qquad Q'_N$$

The flux of neutrons will also be increased five times, so equation (3) must be replaced by

$$M'_N = 5 S\lambda_0 \log_e \frac{U}{C} \qquad \text{.....(5).} \qquad M'_N$$

§ 3. NUMBERS OF THERMAL NEUTRONS

Since there is supposed to be no absorption at velocities above thermal velocity, the number of neutrons which reach that velocity is equal to the number S which are introduced as fast neutrons. The number present in unit volume is therefore ST, where T is the mean life of a neutron after thermal velocity has been reached. If T the number of collisions made before absorption be denoted by P, then P

$$T = \frac{\lambda_0 P}{\bar{c}},$$

and the number Q_T of thermal neutrons per unit volume is given by Q_T

$$Q_T = \frac{S\lambda_0 P}{\bar{c}} \qquad \text{.....(6).}$$

The number crossing unit area (from both sides) per second is M_T where M_T

$$M_T = \frac{\bar{c}}{2} . Q_T = \frac{1}{2} S\lambda_0 P \qquad \text{.....(7).}$$

Equations (6) and (7) are independent of the values of the free path at velocities greater than C. If, as was first assumed in § 2, λ is constant and equal to λ_0, then, from equations (2) and (6), the ratio between the numbers of thermal and non-thermal neutrons is

$$\frac{Q_T}{Q_N} = \frac{C}{2\bar{c}} . P = P \qquad \text{.....(8),}$$

while the ratio of the flux of thermal neutrons to the flux of non-thermal neutrons, from equations (3) and (8), is given by

$$\frac{M_T}{M_N}=\frac{P}{2\log(U/C)} \qquad \text{.....(9).}$$

On the second assumption, that the free path for non-thermal neutrons is five times that for thermal neutrons, each of these ratios is divided by five, so we have

Q'_T

$$\frac{Q'_T}{Q'_N}=\frac{P}{5} \qquad \text{.....(10)}$$

M'_T and

$$\frac{M'_T}{M'_N}=\frac{P}{10\log(U/C)} \qquad \text{.....(11).}$$

Since P is about 80, the number of thermal neutrons is on the first assumption 80 times the number of faster neutrons; on the second assumption this ratio decreases to 16. The ratio U/C is about 6×10^3, and its logarithm is about 8, so the assumption of constant free path gives the flux ratio as about 5; the second assumption would lead to the conclusion that the flux of thermal neutrons is about equal to that of non-thermal neutrons. One would expect the actual value to lie somewhere between these limits; that is to say, thermal neutrons, though not so predominant as when the numbers per unit volume are considered, will constitute a definite majority of the total number which cross any plane in the wax.

§ 4. THE NEUTRONS EMERGING FROM THE SURFACE OF A LARGE BLOCK OF WAX

Many experiments upon the properties of slow neutrons have been made by using the neutrons which emerge from the surface of a block of wax in which is embedded a source of fast neutrons; it is therefore important to consider how the numbers and velocities of the emergent neutrons will differ from those of the neutrons crossing a cavity within the block.

If two semi-infinite blocks are placed face to face so as to leave a thin cavity, the neutrons crossing the cavity may be divided into two classes, (i) those which are making their first transit—that is to say, those which would have emerged from either block had the other block been absent, and (ii) those which have previously made one or more transits—that is, those of class (i) which are scattered back into the cavity after once having emerged from the parent block.

Class (i) is composed of twice the number escaping from a free surface; the neutrons of class (ii) must on the whole be slower than those of class (i), since, until thermal velocities have been reached, scattering involves a decrease of velocity. The number of neutrons escaping from unit area of a free surface must therefore be less than half the number crossing unit area from both directions in the centre of the block, and this decrease will be most marked for the lower velocities.

A proper analytical investigation of the loss of neutrons from a free surface would be difficult, even with the simplifications which have already been adopted, but it is possible to gain some useful information without undue labour by following

out the history of typical neutrons generated at different distances from the surface. If the neutron travels a constant distance λ_0 between collisions, the average component of free path measured normal to the surface is $\frac{1}{2}\lambda_0$. Consider now a neutron starting at a distance $\frac{1}{2}h\lambda_0$ from the surface;* the chance that it shall escape after h having traversed p paths in random directions is nearly† the same as the chance p that in a series composed of $+1$ and -1 in random sequence the sum shall first exceed $+h$ at the pth term. The directions of successive paths are however not independent; this persistence of velocity nearly doubles the average rate at which the neutrons diffuse towards the surface,‡ so we may say that the chance that the random series shall first attain a sum in excess of h at its pth term is equal to the chance that a neutron shall escape after p free paths (i.e., after $p-1$ collisions) from a depth of about $h\lambda_0$ instead of $\frac{1}{2}h\lambda_0$. The process of diffusion from a starting-point situated at h free paths below the surface may therefore be roughly imitated by the tossing of a coin; if the balance of heads over tails first exceeds h when p throws have been made, the neutron has escaped with a velocity corresponding to its having made $p-1$ collisions.

Taking as before 16 collisions as sufficient for the attainment of the critical velocity C, equal to $2\bar{c}$, and 80 further collisions as representing the average life of a thermal neutron, we shall say that if p is 16 or less, the neutron has escaped before reaching thermal velocity; if p lies between 17 and 96, the neutron has escaped with thermal velocity, while if p is greater than 96, the neutron has failed to escape before being captured. With the help of Mr J. R. Tillman I traced out 48 series of this nature, and for each of these found at what value of p the neutron would have escaped if it had started at depths $\frac{1}{2}\lambda_0$, $1\frac{1}{2}\lambda_0$, $2\frac{1}{2}\lambda_0$, ... below the surface. Each of these starting-points is the middle of one of an infinite series of layers, each of thickness λ_0, taken parallel to the surface, so this corresponds to an introduction of fast neutrons at a rate of $48/\lambda_0$ per centimetre of thickness.

The total number of escapes was 360, of which 120 took place before the attainment of thermal velocities and the remaining 240 afterwards.§ If the rate of introduction had been S per cubic centimetre per second, the rate of escape of non-thermal neutrons would therefore have been $120.S.\lambda_0/48$ per square centimetre of surface, and that of thermal neutrons would have been $240.S.\lambda_0/48$. Thus for the neutrons emerging from the surface of a large block we have

$$\text{Flux of non-thermal neutrons} = m_N = 2\tfrac{1}{2}\lambda_0 \quad \text{.....(12)}, \qquad m_N$$

and

$$\text{Flux of thermal neutrons} = m_T = 5\lambda_0 \quad \text{.....(13)}. \qquad m_T$$

The ratio m_T/m_N is therefore about 2 : 1 as compared with the ratio M_T/M_N of 5 : 1 found in § 3 for the neutrons within the block. The proportion of thermal neutrons, though less, is thus still quite comparable with the proportion occurring in the flux of neutrons crossing a cavity within the block. The absolute numbers

* h is not supposed to be integral.

† Some error is of course introduced by the assumption that every component free path is equal to the arithmetic mean.

‡ See Jeans, *Dynamical Theory of Gases*.

§ The simple relation between these numbers is fortuitous.

have decreased considerably; P being taken as 80, equations (7) and (13) show that the flux of thermal neutrons is about eight times less outside than inside the block, while the flux of non-thermal neutrons has decreased about three times.

The flux of neutrons through the surface was next investigated on the assumption that the first 16 free paths were five times as long as those made after 16 collisions had taken place. For this purpose it is only necessary to give a five-fold value to each of the first 16 tosses. The number of non-thermal neutrons escaping rose, of course, five times, being now 600, but this depletion of the outer layers naturally entailed a decrease in the number of thermal neutrons escaping; the number actually fell to 103. Remembering that the use of 48 series corresponds to the introduction of fast neutrons at the rate of 48 per (thermal) free path of thickness, m'_N we obtain for the flux m'_N of non-thermal neutrons corresponding to the introduction of S fast neutrons

$$m'_N = 12\lambda_0 S \text{ approximately} \qquad \text{.....(14),}$$

m'_T and for the flux m'_T of thermal neutrons

$$m'_T = \text{about } 2\lambda_0 S \qquad \text{.....(15).}$$

The decrease in m'_T as compared with m_T is due in great part to the sudden nature of the assumed drop in free path at $u = C$; if the drop is gradual there will be a better chance for the depletion of the surface layers to be made up by the diffusion of the faster thermal neutrons whose free paths would then be of intermediate length; further, there is no reason to suppose that the fall in free path occurs in the immediate neighbourhood of $u = C$, and if it occurs at high velocities the proportion of thermal neutrons emerging will approach more nearly to that obtained on the assumption of constant free path. It is to be concluded, then, that at least a very considerable proportion of the flux of emergent neutrons consists of neutrons of thermal velocities. Whether in any experiment made upon these neutrons the results refer mainly to the thermal or the non-thermal portion of the beam, is a question to which no general answer can be given; it depends upon the sensitivity of the apparatus to neutrons of different velocities.

In table 1 are collected the more important equations which have been derived above, while table 2 gives numerical values of certain important ratios, it being supposed that 80 collisions are made by a thermal neutron before its capture.

§ 5. THE EFFECT OF ABSORPTION OF NON-THERMAL NEUTRONS

The above calculations have been made on the assumption that no neutron is absorbed until it has reached thermal velocity. If a known amount of absorption of faster neutrons does in fact occur, allowance may readily be made for it. For example, a sharp absorption band which removes 10 per cent of the neutrons which have an energy of 100 V. will in every case simply cause a 10-per-cent reduction in the number of neutrons of all lower velocities. The values of m_T/M_T and m'_T/N'_T given above for the inside : outside ratio for thermal neutrons are therefore independent of absorption at velocities above thermal; they depend only upon the

numbers of collisions made before and after thermal velocities have been reached and upon the law connecting free path with velocity.

Table 1. Number and flux of neutrons inside and outside a large block of wax. The rate of introduction of fast neutrons is 1 per cm.^{3} per sec. The values outside the block are for the case of 16 collisions before and 80 after reaching thermal velocities.

	Inside		Outside	
	Free path constant $=\lambda_0$	Free path for non-thermal neutrons $=5\lambda_0$	Free path constant $=\lambda_0$	Free path for non-thermal neutrons $=5\lambda_0$
Number of thermal neutrons per unit volume	$Q_T=\frac{\lambda_0 P}{\bar{c}}$	$Q'_T=\frac{\lambda_0 P}{\bar{c}}$	—	—
Number of non-thermal neutrons per unit volume	$Q_N=\frac{2\lambda_0}{C}$ $=\lambda_0/\bar{c}$	$Q'_N=\frac{10\lambda_0}{C}$ $=\frac{5\lambda_0}{\bar{c}}$	—	—
Flux of thermal neutrons through unit area	$M_T=\frac{1}{4}\lambda_0 P$	$M'_T=\frac{1}{4}\lambda_0 P$	$m_T=5\lambda_0$	$m'_T=2\lambda_0$
Flux of non-thermal neutrons through unit area	$M_N=\lambda_0 \log_e \frac{U}{C}$	$M'_N=5\lambda_0 \log_e \frac{U}{C}$	$m_N=2\frac{1}{2}\lambda_0$	$m'_N=12\frac{1}{2}\lambda_0$

Table 2. Number and flux ratios; 16 collisions made before and 80 after reaching thermal velocity.

	Free path constant $=\lambda_0$	Free path for non-thermal neutrons $=5\lambda_0$
$\frac{\text{Number of thermal neutrons}}{\text{Number of non-thermal neutrons}}$ Inside	80	16
$\frac{\text{Flux of thermal neutrons}}{\text{Flux of non-thermal neutrons}}$ Inside	5	1
$\frac{\text{Flux of thermal neutrons}}{\text{Flux of non-thermal neutrons}}$ Outside	2	$\frac{1}{6}$
$\frac{\text{Flux of thermal neutrons inside}}{\text{Flux of thermal neutrons outside}}$	8	20
$\frac{\text{Flux of non-thermal neutrons inside}}{\text{Flux of non-thermal neutrons outside}}$	3	$2\frac{1}{2}$

§6. COMPARISON WITH EXPERIMENT

(i) A piece of silver foil was placed on the surface of a large block of wax, a source of fast neutrons being placed outside the block in the plane of the surface, figure 1. After a known period of irradiation, the foil was removed and its β-ray activity was measured. The experiment was repeated with a second block of wax, identical with the first, lying on the top of the foil, which was thus at the centre of the composite block. The activity in the second case was greater in the ratio of (13 ± 2) to 1. This lies about midway between the two values 8 and 20 given in table 2 for the inside : outside flux ratio for thermal neutrons, and is higher than either of the two values 3 and $2\frac{1}{2}$ given for non-thermal neutrons. The activity obtained within the block is known to be very largely due to thermal neutrons; see (ii) below. Calculation and experiment agree if it be assumed that thermal neutrons are also mainly responsible for the activity of a specimen of silver exposed outside the block.

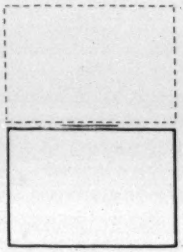

Figure 1.

(ii) If a change be made in the temperature of the walls of a cavity in a large block of wax, the thermal neutrons passing through the cavity have an altered velocity-distribution, and there is a corresponding change in the amount of radioactivity which the neutrons produce in a thin specimen of (for example) silver exposed within the cavity[4]. When the walls are cooled from the temperature of the room to that of liquid oxygen, the change in activity may be as much as 35 per cent for silver, and 50 per cent for copper; it follows that a large fraction of the activity is due to thermal neutrons. When, however, the temperature of the outside of the block is altered, very little change can be observed in the activity of a specimen exposed to the emergent neutrons, although experiments with revolving discs have indicated that some, at least, of the neutrons have thermal velocities[5]. A possible explanation would be that the proportion of thermal neutrons outside a block of wax is actually much less than inside, and constitutes only a very small fraction of the emergent flux, but the present calculations show this to be unlikely. It seems possible that a cold layer at the surface of a block is comparatively ineffective for changing the velocity-distribution of warm neutrons passing through it; an experi-

mental confirmation of this suggestion is described by Mr J. R. Tillman in an accompanying paper[6]. The superior efficiency of a thin-walled enclosure as compared with a single cold layer must be due to the scattering back into the enclosure of neutrons which have already made one transit through the cold wall.

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539.185

NOTE ON THE NEUTRALITY OF THE NEUTRON

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ABSTRACT. From the lack of influence of an electric field upon neutrons of thermal velocities it is shown that the neutron has no electric charge so great as 10^{-7} of the electronic charge.

Dr E. C. Bullard remarked to me recently that some interest might lie in an extremely accurate experimental proof that the neutron is free from electric charge. Chadwick's original proof that neutrons are unaffected by electric fields was made with fast neutrons; now that neutrons having thermal energies are available the sensitivity of such a test can be very greatly increased.

For this purpose I exposed a specimen of silver within a cavity in a large wax block through which neutrons were passing. The resulting β-ray activity was measured, and the experiment was then repeated with the silver at a potential of $+50{,}000$ volts with respect to the wax, and again with the silver at a potential of $-50{,}000$ volts. In no case was there a detectable difference in the observed activity.

Since the majority of the neutrons had kinetic energies of the order of 0·03 electron-volt, a charge of $6 \times 10^{-7} e$ would have prevented them from passing through an opposing potential difference of 50,000 volts, and one-sixth of this charge would have entailed a detectable difference between the observed activities. It is to be concluded that the neutron possesses no charge so great as 10^{-7} that of the electron.

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EXPERIMENTS WITH A NEW TYPE OF RIPPLE TANK

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Demonstration given on March 20, 1936

§ 1. INTRODUCTION

In large-scale ripple-tank work it is customary to demonstrate first with single-pulse disturbances, examining them as they recede from the source. The time of viewing any particular wave is usually short, so that the effects are quickly lost to the observer. It is therefore advantageous to extend the demonstrations to unlimited wave trains and to view the resultant effects stroboscopically. In view of the limited accommodation in most teaching institutions and the relatively high cost of most of the commercial types of projection ripple tanks, an attempt has been made to overcome these drawbacks.

§ 2. TECHNIQUE AND FORM OF APPARATUS

Designed primarily for lecture demonstrations in rooms of medium size, the apparatus is intended to satisfy the following requirements. (*a*) It must be capable of being operated from either a.-c. or d.-c. mains under synchronous conditions or otherwise. (*b*) It must be self-contained and portable with easy adjustments. (*c*) Demonstrations with mercury and water ripples in daylight as well as in a dark room must be possible. (*d*) It must be adaptable for use with modern discharge tubes operated from the a.-c. mains.

For general work the apparatus functions as an autolamp synchronous dual-reed device controlled by the a.-c. mains supply at 50 c./sec. and 100 or 200 V. The addition of a small motor of variable but controlled speed to drive a slotted disc acting as an interrupter, together with a contact breaker actuating the rippler, increases the utility of the apparatus, since means are thus provided for demonstrating progressive waves, in addition to stationary patterns at various frequencies.

The lay-out of the apparatus is shown in figure 1, and a schematic arrangement of the possible methods of use in figure 2.

The apparatus is mounted on two boards A and B, the former being mounted vertically on the latter. A carries the major components of the equipment, and B, the ripple tank C, a levelling table D, and rippler R_2.

For the autolamp dual-reed method the availability of the a.-c. mains is essential to operate two independent reeds R_1 and R_2 in series. R_1 functions as an interrupter cutting off intermittently from the ripple tank the light emitted by a 60-watt auto-

lamp. R_2 carries the necessary iron dippers and so produces ripples in synchronization with the intermittent illumination.

The autolamp is enclosed in a lamp-house mounted on an arm G. Various movements are thus possible for effecting adjustment of the lamp position, which must be such that an image of the lamp filament is formed horizontally and

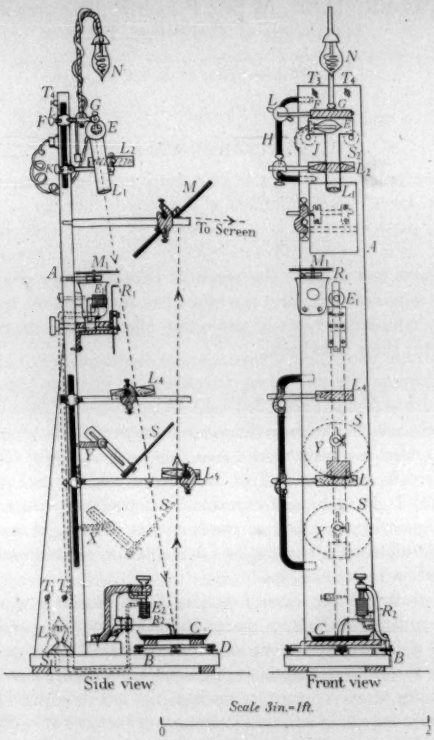

Figure 1. Mounted form of ripple tank.

coincident with the bent end of the reed R_1. This ensures sharp cut-off in the illumination. Both reeds are actuated by electromagnets E_1 and E_2 in series with the a.-c. mains supply, and for control of the current passing through these coils (each consisting of 800 turns) a 100-watt lamp is also included in the circuit together with a controlling switch S_1. The supply voltage is connected to T_1 and T_2. It is essential to operate R_1 at resonance with the mains, but R_2 need not be driven

at such a condition. Provision is also made for varying the air gaps between the reeds and the electromagnets and so effecting control of the amplitudes of the reeds. Whereas R_2 vibrates at a very small amplitude, R_1 vibrates with amplitudes ranging up to 1 cm. The ripple tank consists of a half-plate photographic developing dish, and for water ripples it is preferable to have a plane mirror in the bottom.

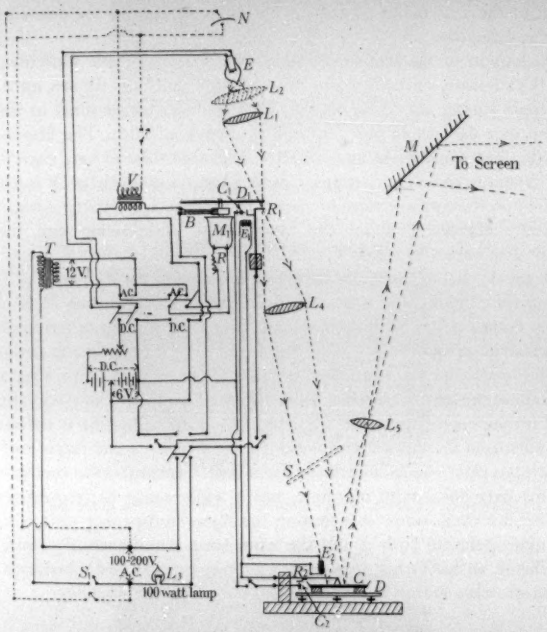

Figure 2. Schematic arrangement showing possible methods of operating ripple tank. E, auto-lamp; N, neon lamp or discharge tube; R_1, interrupting reed; E_1, E_2, electromagnets; R_2, ripple vibrator; L_1, focusing lens ($f=7{\cdot}5$ cm.); L_4, L_5, focusing and projecting lenses ($f=30$ cm.); M, plane mirror; C, ripple tank; M_1, motor driving slotted disc; D, levelling table; S, ground glass screen; T, transformer; B, contact-breaker; C_1, C_2, reed contacts.

By being placed on two pieces of rubber sponge fixed on a levelling table, the tank can be freed from any extraneous vibrations that may arise from possible forced vibrations of the apparatus resulting from vibration of the reeds. Further sound-insulation is effected by using rubber washers between the baseboard and the metal framework carrying R_2. Projection of the ripple images is effected by means of the lenses L_4 and L_5 and mirror M. At a distance of 3 or 4 metres a picture about 3 ft. square is easily obtained with good illumination.

In order to demonstrate progressive waves and the apparent slowing up of the ripples a small motor M_1 (either a.c. or d.c.) is used to drive a slotted disc having four equally spaced radially slots. This disc is mounted alongside R_1 and takes its place for showing progressive waves. A contact-breaker also is attached to the spindle of the motor enabling the equipment to be operated from a d.-c. supply as well as by a.-c., in addition to permitting demonstrations at frequencies other than that of the a.-c. mains. Pieces of watch spring bent to the desired curvature function as reflectors.

The adoption of modern discharge tubes as stroboscopic illuminants in the place of the autolamp only allows for close-up viewing of the ripples, either directly on the ripple surface or via the mirror M. The experiments must in this case be performed in a dark room and the reed R_1 dispensed with. The Osglim lamp is perhaps the most convenient and simplest discharge tube to use, especially when operated from the 200-V. a.-c. supply. Such a lamp is mounted at N and light from it is focused on the ripple surface by means of the lens L_2. Synchronization is thus automatically effected between the intermittent illumination and the ripple-formation. The upper terminals T_3 and T_4, socket J, and switch S_2 are all in series with the 200-V. a.-c. mains, the latter being applied to T_3 and T_4. The plug connecting the Osglim lamp is placed in the socket so that when S_2 is closed the neon lamp flashes at 100 flashes per second. This arrangement of terminals, socket, and switch all in series is readily adaptable to either type of lamp and power-supply. When other discharge tubes are used in place of the Osglim lamp, they are either mounted above the tank or placed at some distance from it on a level with the position occupied by the neon lamp; then light from the discharge tube is reflected by an inclined mirror on the vertical arm down via the lens on to the ripple surface so as to give stroboscopic effects automatically. These discharge-tube methods usually provide for only one length of ripple, but a wider range of frequencies can be attained by the neon lamp, substituting for R_2 a loudspeaker unit carrying the dippers, and operating both it and the neon lamp simultaneously from either a valve oscillator, an oscillating neon tube, a contact-breaker and transformer device, or a thyratron relay source, all of controlled but variable frequency.

§ 3. INSTRUCTIONS FOR METHODS OF OPERATING THE TANK WITH A.-C. MAINS SUPPLY ONLY, AT 100–200 V., AT 50 C./SEC.

(i) For viewing or projecting the stationary patterns at mains frequency, use an autolamp source E, and electrically maintain both reeds R_1 and R_2 by energizing the electromagnets E_1 and E_2 in series with lamp L_3 and the a.-c. supply.

(ii) For viewing directly through the mirror M, and with either a neon-lamp source or some other discharge tube, dispense with reed R_1 as chopper, and operate both the reed R_2 and the lamp source from the 200-V. a.-c. supply, the lamp L_3 again being in series with R_2.

(iii) To distinguish between progressive and apparently stationary ripples, use the motor M_1 and a 6–12-V. a.-c. supply from transformer T, figure 2, and rotate

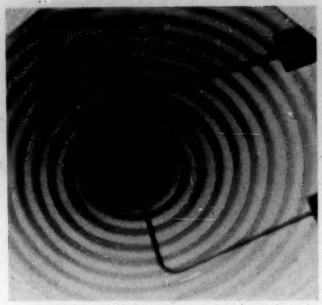

Figure 3. Circular waves in water. Exposure 4 sec. auto-lamp reed method.

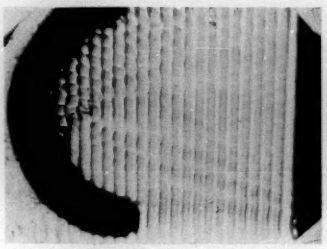

Figure 4. Reflection of plane waves at a concave barrier in mercury. Exposure 1 sec. auto-lamp reed method.

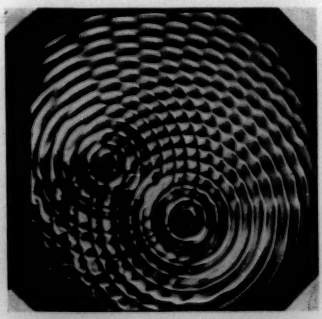

Figure 5. Interference in mercury. B.T.H. neon tube. Exposure 30 sec.

To face page 662

disc D_1, which has four slots, rendering the light from the autolamp intermittent before it falls on the ripple tank. Simultaneously maintain the rippler R_2 by means of a.-c. supply fed through lamp L_3, speed-control of the disc being effected with variable resistance R.

(iv) To demonstrate at correct stroboscopic conditions for different frequencies on a.c., drive the motor from a 6 to 12-V. a.-c. supply, and use the contact-breaker B in series with a 6-V. d.-c. supply and electromagnet E_2 to actuate the rippler R_2. The number of contacts on the spindle is the same as the number of slots in the disc per revolution.

§ 4. INSTRUCTIONS FOR METHODS OF OPERATING WITH D.-C. SUPPLY AT 6–12 V.

(v) Use the autolamp source at 12 V.; electrically maintain R_1 by means of E_1 and contact C_1, and drive R_2 in synchronization with it. E_1 is in series with E_2. Make R_1 function as an interrupter as in method (i). Only one frequency is obtainable, viz. that of R_1.

(vi) To distinguish between progressive and stationary ripples using an autolamp source, maintain R_2 electrically by means of the contact C_2 and a 6-V. supply, and at the same time run the motor at a variable speed so as to drive the slotted disc functioning as the light interrupter.

(vii) For obtaining synchronous effects at all frequencies on d.-c. supply, employ autolamp E, rotating disc D_1 driven by motor M_1, and the contact-breaker B, the latter being in series with the electromagnet E_2. R_2 is thus actuated at frequencies equal to that of the make-and-break current at B. The frequency of ripple-formation is thus controlled by the speed of the motor.

(viii) With the neon-lamp source and for synchronous conditions at all frequencies, couple the lamp to the circuit containing R_2 the rippler and the contact-breaker at B by means of the transformer V. The flashing frequency of the neon lamp is then the same as that of the rippler at all speeds of the motor. A 6-V. d.-c. supply is sufficient in this case.

(ix) For working at a fixed frequency, maintain R_2 electrically by its own make-and-break contact or drive it by R_1, still using the make-and-break method. At the same time couple the neon lamp to this circuit as in method (viii).

(x) To distinguish between progressive and stationary ripples with a neon-lamp source, operate R_2 as in method (ix), running the motor at the same time to actuate the contact-breaker B, which causes the neon lamp to flash at a rate equal to that of the make-and-break. By speeding up the motor the flashing may be brought slowly into synchronization with the ripple-formation.

§ 5. SPECIMEN PHOTOGRAPHIC RESULTS

These are shown in figures 3, 4 and 5. Figures 3 and 4 are typical results for water and mercury obtained by the autolamp dual-reed method, and figure 5 shows the type of result obtainable with the recently developed B.T.H. strobo-

scopic discharge tube. Imperial Process Eclipse plates, speed 650, give satisfactory results.

The illumination provided by other discharge tubes such as the Osira mercury street-lighting, Osira sodium, and neon sign, fluctuate sufficiently in intensity to give reasonably good stroboscopic effects[1]. The cut-off in illumination with all these types of lamps is not so sharp as with either the autolamp or B.T.H. tube. The duration of the flash for each half-cycle of excitation is relatively long also. These effects thus render the definition of the ripple images not so good as those obtained with the autolamp reed device and the B.T.H. tube.

The advantage possessed by the B.T.H. tube as a stroboscopic illuminant is most outstanding and convincing. Owing to the relatively large amount of light available, the adaptation of such a lamp to large-scale ripple-tank work seems highly favourable.

§ 6. ACKNOWLEDGMENTS

My thanks are extended to the B.T.H. Co., Rugby, for loaning me the stroboscopic discharge tube; also to their research staff for the kindly interest taken in this section of the work.

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538.22:546.711

THE MAGNETIC PROPERTIES OF MANGANESE HEATED IN NITROGEN

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AND

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ABSTRACT. The combination of amorphous manganese with nitrogen has been studied over the temperature range 300–1000° C., and it has been found that ferromagnetic compounds are formed at much lower temperatures than had been reported previously. The magnetic hysteresis phenomena exhibited by these compounds have been studied, and their ferromagnetic Curie points have been determined by a simple method. An X-ray study of their structures has also been made; it is found that the existence of ferromagnetism can be associated with a γ phase of manganese with a slightly enlarged lattice constant; the function of the nitrogen is not completely understood.

§ 1. INTRODUCTION

During an investigation of magnetic properties of amorphous manganese Bates and Reddi Pantulu[1] observed that some of the specimens exhibited traces of ferromagnetism when the amalgams from which they were prepared had been in contact with air for a longer time than was desirable. Manganese specimens made under the best conditions were definitely paramagnetic and did not show any traces of ferromagnetism. It is well known that manganese readily combines with many non-magnetic elements to give ferromagnetic substances, and it appeared likely that some of the manganese used in these experiments had combined with atmospheric nitrogen.

In 1909 Wedekind[2] obtained three nitrides of manganese, Mn_3N_2, Mn_5N_2, Mn_7N_2, prepared at various temperatures between red heat and that of the oxyhydrogen flame; he found that the higher nitrides were strongly magnetic and the lower nitrides feebly magnetic. Later, Ishiwara[3] used Kahlbaum manganese and suggested that manganese formed two compounds and a solid solution with nitrogen in the temperature interval 600–1600° C. All three were found to be ferromagnetic and were distinguished by their thermomagnetic properties and their Curie points T_f, which are given in table 1.

More recently Ochsenfeld[4] has made magnetic and X-ray studies of the manganese-nitrogen compounds obtained by heating manganese in nitrogen at 1100° C. and he has attributed the observed ferromagnetism to the solution of nitrogen in the γ phase of manganese. The lattice constant and the intensity of magnetization increased with increase in nitrogen concentration. Ochsenfeld obtained an atomic

concentration of as much as 12 per cent and found the lattice constant to be increased from 3·80 to 3·86 A., while the maximum value of the intensity of magnetization was about 40 c.g.s. units. He found the Curie point for one typical
H_c specimen to be 500° C., its coercive force H_c at room-temperature being 200 oersteds. He was unable to obtain magnetic saturation even with fields of 650 oersteds; in

Table 1

Compound	Preparation	Curie point T_f
Mn_3N_2	Heated in nitrogen from 1200 to 1600° C.	One at 50° C. One at 750° C.
Mn_5N_2	Heated in nitrogen from 600 to 1300° C.	500° C.
Mn_7N_3	Heated in NH_3 at 1450° C.	750° C.

his experiments the demagnetizing factor was negligibly small. An X-ray study of a large number of specimens, prepared by heating finely powdered Geyler manganese to a high temperature in a stream of ammonia or nitrogen, has been made by Hägg[5]. He found that the specimens so prepared were not homogeneous, and they were therefore maintained for some days at a temperature of 400 or 600° C. in an evacuated sealed tube to make them homogeneous.

It will thus be seen that all the previous investigators studied the behaviour of compounds of manganese and nitrogen prepared at high temperatures only. It is equally important to know whether ferromagnetic compounds can be formed at relatively low temperatures. Accordingly the following experiments were carried out, and have provided much additional information concerning the temperature range 300–1000° C.

§ 2. PREPARATION OF SPECIMENS

Manganese amalgam was prepared by electrolysis in the manner previously described[4]. It was quickly transferred from the bath to the pyrex glass apparatus shown in figure 1, which was then evacuated and heated to 300° C. to drive off the mercury, which was condensed and collected in a water cooled bulb. After most of the mercury vapour had been driven off, a mercury pump and liquid-air trap were used to remove the last traces. The water-cooled bulb was then sealed at a constriction and removed. A three-way tap connected the pyrex apparatus either to a hyvac pump or to a nitrogen cylinder. The nitrogen was first passed over heated copper filings, to remove any oxygen present, and then through condensers surrounded by water and liquid air, respectively, to remove water vapour. A simple mercury barometer tube was used in the nitrogen circuit to act as a safety valve and also as a pressure-indicator.

Specimens were prepared by allowing the purified nitrogen to remain in contact with manganese maintained at chosen temperatures, 300, 400, 500 and 550° C. for an hour in each case, after which the manganese was allowed to cool slowly in contact with nitrogen. Some of the compounds thus formed were forced into one

of the small tubes, the pyrex glass beads in the apparatus being used for this purpose. The apparatus was then evacuated and the filled tube was sealed and detached. The remaining manganese was heated anew in the presence of nitrogen and kept at another higher fixed temperature for 1 hour, the whole procedure being repeated until all the tubes were filled. For specimens treated at higher temperatures, 750, 800, 900 and 1000° C., a quartz apparatus similar to the pyrex apparatus of figure 1 was used.

§3. MAGNETIC EXPERIMENTS

The Gouy method for the investigation of the magnetic properties of these specimens was successfully used in the case of that treated at 300° C. Some of the remaining specimens were so ferromagnetic that lateral displacements made such measurements impossible, and consequently a ballistic method was employed. A water-cooled solenoid with eight layers, each of 302 turns, was used as the magnetizing solenoid. Two equal coils of double-silk-covered wire, s.w.g. 36, were wound on similar ebonite formers. These were placed axially inside the solenoid and connected in opposition so that on reversal of the current in the solenoid only a small deflection was observed with a ballistic galvanometer connected to the coils. One of the coils was placed in the middle of the solenoid and the other some 5 cm. below it. A smaller compensating coil in series with the first two was used for fine adjustment to give complete compensation when a current of 10 amperes was reversed in the solenoid. The magnetizing solenoid was supplied from a 120-volt battery of accumulators, and suitable resistances by which the current could be reduced in steps from 10 amperes were used. The specimen under examination was placed in the ebonite coil in the middle of the magnetizing solenoid, and the hysteresis cycle was obtained in the usual way by observing the throw of a ballistic galvanometer for known changes of current.

In order to calibrate the ballistic throw in terms of the induction in the specimen, a test solenoid of 200 turns was wound on a glass tube 6·2 cm. long, of the same diameter as the specimen, and placed in the region formerly occupied by the latter. A known current was then reversed through this test solenoid and thus the deflection of the galvanometer corresponding to the reversal of a known number of lines could be observed. In order to take account of the packing density of the specimens, the specific magnetization or magnetic moment per gram was found by making the appropriate weighings in each case.

The ferromagnetic Curie points of the specimens were determined by a very simple method; the necessary apparatus is shown in figure 2. A thick-walled copper tube was coated inside and out with Insulate cement and wound non-inductively with two layers of nichrome strip, the successive layers being insulated by the same cement. The furnace was provided with a quartz side tube *P*, and with circular end pieces of asbestos furnished with mica windows. A thermocouple *Th* was used to measure the temperature of the furnace. The latter was placed directly above the poles of an electromagnet cooled by passing water through the metal tubing *pp*.

Over *P* was slipped the tube *Q* which carried the torsion head *T*. From *T* a

long and stiff quartz fibre was suspended from a short length of weak phosphor-bronze strip. A sample of a compound was packed and sealed inside a quartz tube about 3 cm. long and 2 mm. in internal diameter. The tube and its contents were provided with a thin platinum wire loop which was hooked on to the end of the quartz fibre. The loop was rigidly connected to the quartz tube and to the quartz hook by Insulate cement. The suspended system was then given a preliminary heating to cause the cement to set hard.

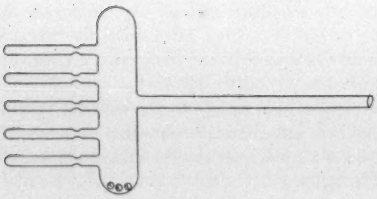

Figure 1. Apparatus for preparation of specimens.

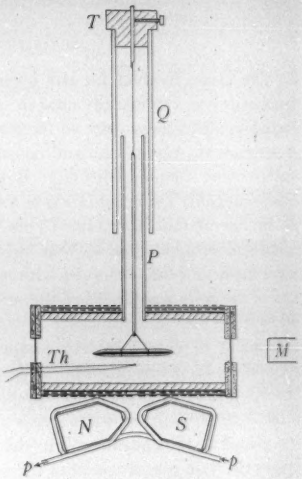

Figure 2. Apparatus for determination of Curie points.

The magnet was excited by a current of 5 A., causing the specimen to be magnetized strongly. The current was then reduced to 0·5 A., sufficient to provide a constant field of some 125 oersteds in which the specimen was made to oscillate. Since the phosphor-bronze suspension was very weak, the reciprocal of the square of the period t of oscillation was almost directly proportional to the product of the magnetic moment and the applied field. A series of values of the period of oscillation were obtained at different temperatures under these conditions. The curves obtained by plotting $1/t^2$ against the corresponding furnace temperatures are shown in figure 3, arbitrary units being used to give a common axis. The very marked changes in $1/t^2$ enables us readily to fix the Curie points with a degree of accuracy sufficient for the present work. The provision of the long quartz fibre ensured that the torsion constant of the suspension should not appreciably change with furnace temperature, and these arrangements were very satisfactory indeed up to temperatures of 600° C. This is well shown by the curve labelled Ni in figure 3, which represents the curve obtained when a pure nickel rod, 3 cm. long, was placed inside a quartz tube and used as a specimen. In this case a field of some 50 oersteds

was employed in the measurement of t. The Curie point obtained from this curve is 354° C., which compares favourably with the accepted value 356 ± 2° C.

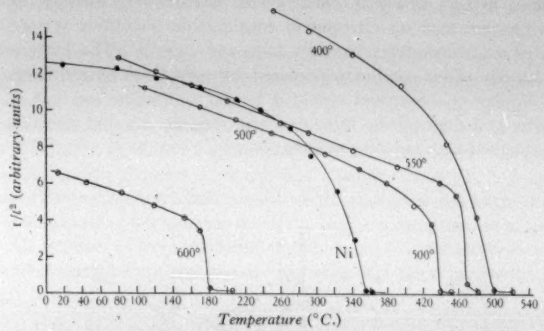

Figure 3. Curves for determination of Curie points. ○ manganese heated in nitrogen; ● nickel for comparison.

§4. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the Gouy measurements of the specimen prepared at 300° C. gave a linear variation of k with $1/H$, showing clearly that a small but definite amount of ferromagnetism existed. It is felt that although this might have been increased with longer time of preparation, it is so small that the possibility of its being due to a trace of iron impurity cannot be excluded. Hysteresis curves were obtained for the specimens prepared at 400, 500, 550, 600° C., but it was impossible to obtain curves for the remaining specimens. The curve for the specimen prepared at 400° C. is shown in figure 4, where the intensity of magnetization per gram is plotted against the applied field. No correction was made for demagnetization factor, for although the pyrex tubes were of internal diameters 0·44, 0·45, 0·44, 0·48, 0·36 cm., the observed intensity of magnetization was in every case too small to warrant the application of such correction. The relevant data are given in table 2.

Table 2

Temperature during preparation (° C.)	300	400	500	550	600
Coercive force (oersteds)	—	153·4	109·6	116·9	73·0
Specific magnetization in a field of 730 oersteds	($0{\cdot}7\times10^{-3}$)	6·98	8·76	9·49	1·21
Ferromagnetic Curie point (° C.)	—	500	430	470	182

On comparing these hysteresis curves it was seen that in all cases magnetic saturation was not obtained even for a field of 730 oersteds, and there were progressive differences in the maximum values acquired in that field and in the coercive forces, as recorded in the above table. The specimens prepared at higher

temperatures of 700–900° C. in the quartz tubes showed no measurable magnetization when tested by the ballistic method, in spite of the fact that these specimens were allowed to cool slowly in contact with nitrogen. Ochsenfeld found that Geyler manganese took up nitrogen in considerable quantities at 1060° C. but re-emitted it at temperatures between 1300 and 1320° C. The hysteresis curve obtained for one of his specimens prepared between these temperatures was remarkably similar to the curves obtained by us; saturation was not reached at 650 oersteds, and the coercive force was 200 oersteds, a value somewhat higher than that obtained with our preparations.

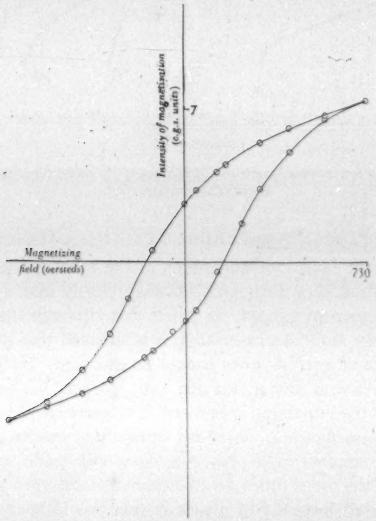

Figure 4. Hysteresis curve for specimen of manganese heated in nitrogen at 400°.

X-ray photographs were taken of the samples of amorphous manganese heated respectively to temperatures of about 300, 400, 500, 550, 600 and 1000° C. in contact with nitrogen. The powders were enclosed in very thin tubes of Lindemann glass and photographed with copper rays by means of a circular camera. A visual comparison of the photographs clearly revealed the existence of structural differences between the specimens, in fact, the photographs fall into three groups; the first comprises only that of the 300°-C. specimen, the 400, 500 and 550°-C. specimens account for the second group, whilst the photographs of the 600 and 1000°-C. specimens have been allocated to the third group. Each group contains photographs either exactly alike or very similar, but differing markedly from those of other groups. Such a division amongst the specimens is in general agreement with the magnetic observations, according to which the second group contains just those

specimens which exhibit ferromagnetic properties to the greatest extent. Further photographs will be taken later with a more suitable apparatus to attain a greater measure of accuracy, as that in use was not of the design best suited to this type of specimen.

The results of each photograph will be discussed in turn, beginning with that referring to the lowest-temperature specimen. This photograph is representative of a simple cubic structure of cube-edge 6·28 A., corresponding therefore to manganese in its β phase; no γ phase lines were visible. All photographs of the second group of specimens exhibited a superposition of two structures, the simple cubic corresponding to the β phase of manganese already mentioned, together with a face-centred cubic structure allied possibly to the face-centred tetragonal cell of the γ phase of manganese. Considering firstly the simple cubic structure of the β phase, the cell-size appears to have increased slightly to 6·38 A. for all these specimens; the reflections arising from this are all very weak. On the other hand the γ phase is strongly marked and gives rise to the reflections (111) st., (200) st., (220) st., (311) v.st., (222) m/w, (331) w, and (420) w; the cell-size is 3·84 for the 400°-C. specimen and 3·86 for the 500 and 550°-C. specimens. These values are similar to those found by Ochsenfeld for specimens treated at much higher temperatures and exhibiting grating-sizes large compared with the non-magnetic nitrogen-free γ phase of manganese, and correspond to some extent with the results of Hägg for what he terms the ϵ phase.

The outstanding feature of the photographs of the last group, comprising the 600 and 1000°-C. specimens, is their much greater complexity and the general weakness of the lines; to permit of interpretation, they need the higher accuracy in view. The photographs, though differing in detail, show a marked similarity to one another. They differ entirely from those of previous groups and do not show any trace of the enlarged γ phase; this is of interest particularly as far as the 600°-C. specimen is concerned, for this still displays ferromagnetic properties; longer exposures will disclose whether this phase is entirely absent.

It is clear that the behaviour of manganese in contact with nitrogen presents a problem of some complexity. The present study shows that finely divided manganese reacts far more readily at comparatively low temperatures to form ferromagnetic substances than was previously believed. The function of the nitrogen cannot be deduced from the X-ray observations, although the expansion of the lattice suggests that the nitrogen acts merely by separating manganese atoms without forming a definite chemical compound. The experiments with the 300°-C. specimen definitely suggests that the ferromagnetic impurity in this case is iron introduced during the electrolysis, and provides additional evidence for the view that pure manganese is not ferromagnetic.

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REVIEWS OF BOOKS

Molekülstruktur, von Dr H. A. Stuart, Struktur und Eigenschaften der Materie, XIV. Pp. x+388. (Berlin: Julius Springer.) RM. 32.

Quantenmechanik der Materie und Strahlung, *Handbuch d. Radiologie*, Band VI, 2 Auflage, Teil II: *Moleküle*. (Leipzig: Akademische Verlagsgesellschaft.) RM. 54.

There have been great advances in our knowledge of the structure of molecules during the last few years owing to the discovery of new experimental methods of attack. The diffraction of X rays and of electrons by molecules has been used to determine the disposition of individual atoms in molecules, Raman spectra and infra-red spectra have yielded information as to the internal vibrations of these atoms in relation to one another, and in some cases measurements of dipole moments have been used to infer the degree of relative motion of groups within a molecule. In view of these advances in so many different but related fields it is useful to have a connected account of the information now available as to the structure of molecules, and nowhere can a better or more complete summary of these advances be found than in the book by H. A. Stuart.

After a brief review of present theories of the forces which hold molecules together, of modern theories of valency and of the new conception of the nature of single and double bonds, the author goes on to describe methods of determining the outer forces which molecules exert on one another. From the external properties he passes to the internal properties and gives experimental details of methods of registering the scattering of X rays and electrons by gases, ending with a summary of the internal dimensions of a number of inorganic and organic molecules obtained by such methods.

There is an authoritative account of methods of determining dipole moments, as would be expected of an acknowledged expert in that field. The chemist interested in stereochemistry will find the discussion of the structure and internal motion of molecular groups most informative.

The optical properties of molecules as indicated by the Kerr and other effects are described at considerable length—probably at too great length, seeing that most of the work described is classical and has been dealt with adequately many times. The second half of the book is concerned mainly with the vibrations of molecules and with the methods by which they are determined and assigned. The selection rules of infra-red spectra and Raman spectra are given, and the characteristic features of these two complementary methods are summarized. Details of a large number of simple and polyatomic molecules are recorded and altogether this section is extremely useful for purposes of reference. The book concludes with tables of the size, structure, fundamental frequency and other properties of diatomic, triatomic and polyatomic molecules.

The reviewer can confidently recommend Dr Stuart's book as a clear, reliable account of an important subject. It is profusely illustrated, contains comprehensive references to the literature, and bears the signs of a careful and thorough piece of work.

The other book under review consists of a series of articles by experts on the properties of molecules. It covers very much the same ground as the book by Dr Stuart but the accounts of the separate subjects, while more detailed and technical, are less coordinated than his. The theory of molecular spectra is given in a general, non-mathematical way by R. de L. Kronig, who deals with the quantum numbers and method of description of rotational, vibrational and electronic states. This leads him to a discussion of predissociation and other related phenomena associated with molecular spectra.

There is an authoritative article by P. Debye and H. Sack on the electrical properties of molecules such as induced polarizabilities, dipole moments, and the effect of these on

dispersion in gases and fluids, together with a learned discussion of the Raman effect by G. Placzek (pp. 209–374). This is the most complete and thorough discussion of the theory of Raman scattering that the reviewer has seen, for it contains an account of the symmetry properties of molecules and of the selection rules for each class of symmetry, which is nowhere else accessible.

Dr F. Block contributes an article on the molecular theory of magnetism with sections on the diamagnetism and paramagnetism of atoms and molecules and the ferromagnetism of the iron group of solids. The quantum theory of valency is dealt with by W. Heitler. After describing the quantum numbers of atoms and molecules, he develops the theory of the interaction of unsaturated atoms and shows the importance of spin in determining the magnitude of the forces between atoms. This article was, however, completed some time before publication and some of the later developments of the theory are not included.

The present volume, containing as it does a number of scholarly articles by well-known authorities, worthily maintains the standard set in earlier volumes of the Handbook and will be welcomed by all those interested in the rapidly growing subject of molecular structure.

J. E. L.-J.

Visibility in Meteorology. The Theory and Practice of the Measurement of the Visual Range, by W. E. Knowles Middleton, Toronto. Pp. viii + 104. (Oxford University Press and The University of Toronto Press, 1935.) 8*s*. 6*d*. net.

"Stultus est qui fructus magnarum arborum spectat, altitudinem non metitur." These words apply to no science more fitly than to visibility; indeed it would not be exaggerating to say that the usefulness of visibility statistics, if not the very science of forecasting visibility, has been seriously hampered by the lack of precise methods of measurement based upon a clear understanding of the different forms and aspects of visibility and their relations. Yet this book is the first to co-ordinate and review the all-too-small amount of past work on the subject. The author has not merely filled a gap in our literature, he has produced a readable and comprehensive book, of value both to the general reader and to the specialist.

The accounts given of past researches are clear, concise and reliable. The elucidation of the subject is, however, so incomplete, and the question "What are the best means of measuring visibility" is so controversial, that it is only to be expected that views should occasionally be expressed which can only be regarded as personal and not generally established. It is in no carping spirit that it is pointed out that the author's views on "a rational scale of visual ranges" will probably not be acceptable to many persons interested from points of view different from that of the author. Nevertheless, the avowed purposes of the book—"to put measurements of visual range on a more rational basis, to improve the techniques of observation, and to stimulate investigation"—are well served.

M. G. B.

The Revolution in Physics, by Ernest Zimmer. Translated by H. S. Hatfield. Pp. xiv + 240. (London: Faber and Faber, Ltd.) 12*s*. 6*d*. net.

That part of the science of physics which deals with fundamental entities, their natures and their interactions, is growing very rapidly and is of great interest to scientist and to layman. This excellent survey of the experimental discoveries and of the theories accompanying them is a welcome addition to the immense body of literature on physics. The treatment throughout the book is non-mathematical and, while details of experimental technique are purposely omitted, the diagrams and photographs supplied are sufficient to indicate clearly the general nature of the evidence on which modern views are based.

After some discussion of the nature of matter and light according to classical physics,

the reader is presented with an account of the quantum hypothesis and its application in the study of the structure of atoms. The necessity for the introduction of new ideas and assumptions is made very clear and the subsequent developments of the wave theory which have led to the present-day conceptions of a wave-model atom are lucidly described.

The last chapter on "Science and philosophy" indicates how the new physics offers some contribution towards the solution of problems which have stirred the thoughts of philosophers throughout the ages. The position to-day may be summarized by such quotations as "the world is more mysterious than we imagined in the days of classical physics". One may be "a pessimist as regards the possibility of understanding the inward nature of the world, but the scientist is an optimist, for his more modest goal is simply to find symbols to describe the world of experience and to test their power of predicting new experimental facts". "We climb one peak and make a short rest, but already the next and higher one awaits us."

Author and translator are both to be warmly congratulated on the production of a book which not only will appeal to a very wide public but will, on account of its clarity of exposition, be enjoyed by all who read it.

In one paragraph the adjective "western" is used to qualify the noun "science". L'art n'a pas de pays! Nicht wahr? J. H. B.

Soviet Science, by J. G. CROWTHER. Pp. x+342. (Kegan Paul, Trench, Trubner and Co., Ltd.) 12*s*. 6*d*. net.

This excellent book is well worth reading. It is based on first-hand knowledge of the work which is being carried out in the various institutes described. The author is a frequent visitor to the U.S.S.R., and has acquired a thorough knowledge of the way in which the reconstruction of society in that country has affected the scientific work which is being carried out there; moreover he possesses accurate information concerning recent developments in science. The opening chapter on dialectical materialism is intended to form a background for the proper understanding of the developments described in the remainder of the book. In this chapter and in many other parts of the book will be found statements which will repay the most careful thought of those responsible for the organization of science in this country and its relation to our own society. For example, the various groups of research workers are responsible for the economics of their work and have to keep a record of all the expenditure incurred, a practice that might be followed with advantage in many institutions in this country. An interesting chapter on conferences contains some useful suggestions. The care of the various workers is described, and such facts as that "persons who work with X rays receive an addition to their annual holidays and are entitled to an extra daily milk ration free of charge" are worthy of note. The author makes some pointed remarks on the throttling effect of patent monopolies in the western countries. In one laboratory controlled by the war department the "visitor is followed at a distance of two paces, even through wind tunnels, by a pair of armed guards". In the chapter on biology we read the curious statement that "from the belief that physics is the more fundamental science, many Western European writers conclude that God is a physicist or a mathematician". Some parts of the book are rather in the nature of a catalogue and the lists of researches being carried out might have been more conveniently placed as appendices.

The book is well printed and contains 16 plates and an index. We have only noticed two or three minor misprints which no doubt will be corrected in future editions.

Whether the reader is interested in the relation of science to the structure of society or in the development of science itself, or even in the organization of some technical institute, he will find something in this book which will not only interest him but will also be of value to him in his work. H. R. L.

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THE SIZE OF ATMOSPHERIC NUCLEI: SOME DEDUCTIONS FROM MEASUREMENTS OF THE NUMBER OF CHARGED AND UNCHARGED NUCLEI AT KEW OBSERVATORY

BY H. L. WRIGHT, M.A.

Received January 23, 1936. *Read in title April* 4, 1936

ABSTRACT. The first object of this paper is to set out formulae to be used in determining the size of condensation nuclei from observation of the concentration in the atmosphere of charged and uncharged nuclei and observation of the numbers of small ions of either sign. It is well known that ratios of the combination coefficients which specify the rates of combination of small ions with charged or uncharged nuclei can be deduced from such observations. In the present analysis the following additional principles are assumed. (1) The combination coefficients are related to w, the mobility of small ions by Whipple's hypothetical equation

$$\eta_{12} - \eta_{10} = 4\pi e w,$$

and (2) combination between small ions and uncharged nuclei are produced solely by collisions due to the random Brownian movements of the small ions.

On the assumption that a small ion is equal in mass to eleven molecules of water it is deduced from Scrase's observations at Kew Observatory that so long as the relative humidity is less than 80 per cent the radius of a nucleus is approximately 3×10^{-6} cm. With higher humidities the radii are larger, at 82 per cent $4{\cdot}2 \times 10^{-6}$ cm. and at 89 per cent $4{\cdot}5 \times 10^{-6}$ cm. In the last section of the paper Köhler's theory of the growth of nuclei in an atmosphere in which humidity increases is applied, and on the assumption that the hygroscopic nuclei at Kew are of diluted sulphuric acid, it is found that in summer the mass of the acid in a nucleus is about 18×10^{-17} g., the corresponding mass in winter being 12×10^{-17} g. If the predominant nuclei are of common salt or of nitrous acid these estimates must be halved to give the mass of salt or of the latter acid in a nucleus.

§ 1. INTRODUCTION

LITTLE is known in detail of the size of the hygroscopic nuclei found in the air or of the changes in size which they undergo with varying conditions of humidity. It is fairly evident that as the air becomes damper the nuclei will grow larger, and, as Köhler has shown[1], some idea of the form of the variation in

their size with relative humidity may be obtained from thermodynamical considerations.

It is also evident on general grounds that the small ions in the air, which move with high velocities, are more likely to collide with a large nucleus than with a small one, and so the frequency of recombinations between small ions and nuclei is another indication of the size of the nuclei. The frequency of recombinations cannot however be measured directly but has to be inferred from measurements of other quantities. Whipple's theory[2] of recombination coefficients provides a very simple method of inferring the frequency of recombinations as it leads to a relation between the recombination coefficients and a quantity which is easily measured,

N_0, N viz., the ratio N_0/N, where N_0 denotes the concentration of uncharged nuclei and N denotes the concentration of charged nuclei of one sign.

The publication, in a recent paper by Scrase[3], of a curve showing how the ratio N_0/N at Kew Observatory varies with the relative humidity presents an opportunity of co-ordinating these two lines of approach to the problem of determining the size of nuclei. Values of the radius of the nuclei may be derived from those of N_0/N, and the curve given by Scrase may be used to determine the association between the radius of the nuclei and the relative humidity at Kew. This association may then be compared with that which is to be expected on thermodynamical grounds. This in brief is the aim of the present paper.

Whipple's theory, on which the derivation of the recombination coefficients from the ratio N_0/N is based, is expressed mathematically by the following equations:

$$\eta_{12}-\eta_{10}=4\pi e w_1, \quad \eta_{21}-\eta_{20}=4\pi e w_2 \qquad \ldots\ldots(1{\cdot}1),$$

w_1, w_2 where w_1, w_2 denote the mobilities of the positive and negative small ions respectively, η_{12}, η_{21} denote the recombination coefficients between small ions and η_{12}, η_{21} oppositely charged nuclei, η_{10}, η_{20} denote the recombination coefficients between η_{10}, η_{20} small ions and uncharged nuclei, and e denotes the elementary electric charge. e

Values of the radius of the nuclei may be derived from those of η_{10} by use of the following formula:

$$\eta_{10}=\pi r^2 U \qquad \ldots\ldots(1{\cdot}2),$$

r, U where r is the radius of the nuclei, and U is the average value of the Brownian velocity of small ions due to thermal agitation. This formula, which may conveniently be called the Brownian hypothesis, is obtained from considerations of the Brownian movement of the small ions as set forth in § 4 below.

In a paper[4] published in the *Philosophical Magazine* in July 1934, Dr Harper obtained formulae expressing η_{12} and η_{10} in terms of the radius of the nuclei and the mean free path of the small ions. Harper has subsequently corrected[5] his formulae for a numerical error which occurred in his previous work, but he informs me that he is not satisfied with the mathematical approximations which he used and that he is now recalculating η_{10} by exact methods. Pending publication of the new formulae it has been thought better to make no use of Harper's original formulae in the present paper. Accordingly our calculations will be based on Whipple's assumption and the Brownian hypothesis.

§ 2. THE RADIUS OF THE NUCLEI AS DEDUCED FROM THE KEW OBSERVATIONS

The diagram given by Scrase, showing the variation in the total concentration Z of nuclei and in the ratio N_0/N with relative humidity, is reproduced in figure 1, and the values corresponding to the points in the diagram are tabulated in table 1. Each value is derived from the mean of between 10 and 12 individual observations of Z and N_0 with the Aitken nucleus counter, N being defined by the equation

Z

$$Z = N_0 + 2N.$$

§ 3. VALUES OF η_{10}

The first step in evaluating the radius of the nuclei is to calculate the values of the recombination coefficient η_{10}. These may be found from the formula

$$\eta_{10} = 4\pi e w_1 \frac{1 + fN_0/N}{(N_0/N)^2 - 1} \qquad \ldots\ldots(3{\cdot}1),$$

where $f = n_2 w_2 / n_1 w_1$, n_1 and n_2 denoting the concentration of positive and negative small ions respectively.

f, n_1, n_2

This formula follows immediately from (*a*) the equilibrium equations for nuclei, viz.,

$$\eta_{10} n_1 N_0 - \eta_{21} n_2 N_1 = 0 = \eta_{20} n_2 N_0 - \eta_{12} n_1 N_2,$$

where N_1 and N_2 denote the concentration of positive and negative large ions respectively, (*b*) Whipple's formulae (1·1), viz.,

N_1, N_2

$$\eta_{12} - \eta_{10} = 4\pi e w_1, \quad \eta_{21} - \eta_{20} = 4\pi e w_2,$$

and (*c*) the assumption that

$$N_1 = N_2 = N,$$

which is justified in the present instance by the fact that at Kew the space charge is always found to be small. From observations of the potential-gradient at various heights Scrase has shown[6] that on the average the space charge at Kew corresponds almost exactly to the excess of positive small ions, about 60 per cm.^{3} In still air, when the small-ion content is low, the space charge is rather larger and corresponds to an excess of about 300 positive ions per cm.^{3}; even if this were entirely due to large ions, the concentration of which in quiet conditions at Kew is about 30,000 per cm.^{3}, the ratio N_1/N_2 would only be 1·02. Hence, except possibly when individual cases are under consideration, the assumption that N_1 and N_2 are equal at Kew is not likely to lead to serious error.

In an earlier paper[7], in which I obtained a formula relating N_0/N to the radius of the nuclei, it was assumed that there was equality between the frequencies with which small ions of either sign combine with uncharged nuclei. It may be shown that this is equivalent to assuming that the value of f, or $n_2 w_2 / n_1 w_1$, is unity. Such an assumption is not supported by observations at Kew, where although the mobilities w_1 and w_2 remain fairly constant, equal to 0·98 and 1·05 cm./sec. per V./cm. respectively, the ratio n_2/n_1 on the other hand is subject to a systematic variation with nucleus content, decreasing from 0·76 when the concentration of nuclei is 11·8 per mm.^{3} to 0·65 when the concentration is 62·4 per mm.^{3} There are indications that with higher concentrations of nuclei, that is when the values of n_1 and n_2 are

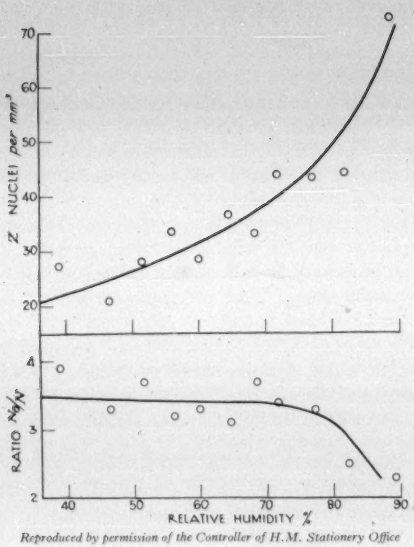

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Figure 1. Variation in nucleus-content and in the ratio N_0/N with relative humidity. (Kew Observatory. 15 h. G.M.T.)

Table 1. Variation in nucleus-content and in the ratio N_0/N with relative humidity at Kew, and deduced values of the recombination coefficient η_{10} and the radius of the nuclei

Relative humidity (per cent)	39	46·5	51·5	56·1	60·1	64·6
Concentration of nuclei per mm³	27·1	21·0	28·2	33·5	28·5	36·7
Ratio N_0/N	3·9	3·3	3·7	3·1	3·3	3·1
Recombination coefficient η_{10} deduced from Whipple's formulae (10^{-6} cm³/sec.)	0·49	0·61	0·52	0·66	0·63	0·68
Radius of nuclei r deduced from Brownian hypothesis (cm. $\times 10^{-6}$)	3·0	3·3	3·1	3·5	3·4	3·5
Values of Q deduced from thermodynamical equation (cm³ $\times 10^{-18}$)	17	22	15	19	17	17
			Mean 18			
Relative humidity (per cent)	68·6	71·8	77·2	82·2	89·2	
Concentration of nuclei per mm³	33·1	44·0	43·6	44·3	72·3	
Ratio N_0/N	3·6	3·4	3·3	2·5	2·3	
Recombination coefficient η_{10} deduced from Whipple's formulae (10^{-6} cm³/sec.)	0·53	0·59	0·62	0·97	1·09	
Radius of nuclei r deduced from Brownian hypothesis (cm. $\times 10^{-6}$)	3·1	3·3	3·4	4·2	4·5	
Values of Q deduced from thermodynamical equation (cm³ $\times 10^{-18}$)	11	10	10	15	12	
			Mean 12			

small, the value of n_2/n_1 may be still lower, but in these circumstances observations of n_1 and n_2 are not very reliable.

As however the value of η_{10} deduced from equation (3·1) is not highly sensitive to changes in the value of n_2/n_1, an inaccuracy of 0·06 in n_2/n_1 leading to an error of only 6 per cent in η_{10}, we may here adopt an average value of n_2/n_1 equal to 0·70 without introducing serious error. We shall therefore take

$$f = 0{\cdot}70 \times 1{\cdot}05/0{\cdot}98 = 0{\cdot}75.$$

The values of η_{10} obtained from those of N_0/N by use of the formula (3·1) are shown in table 1. The scatter in these values, which is due to the scatter in the values of N_0/N, might have been avoided by utilizing smoothed values of N_0/N read from the curve in figure 1, but it was considered that the use of values of N_0/N derived from actual observations was preferable to working with hypothetical values obtained from a curve which it is not yet possible to locate with precision.

The values of η_{10} shown in the table are of the same order of magnitude as those deduced by Scrase from formula (3·1) with exact values of the coefficient f, and discussed by him in his paper; the point to which attention may be drawn here is the apparent absence of systematic variation until humidities of about 80 per cent are reached.

§ 4. THE BROWNIAN HYPOTHESIS

Values of the radius of the nuclei may be deduced from those of η_{10} by use of the Brownian hypothesis (1·2) which may be formulated as follows. According to the simple view of the recombination coefficient between small ions and uncharged nuclei, forces due to electrical attraction may be ignored and only random collisions due to thermal agitation need be considered. The nuclei, being very large and inert compared with the small ions, may be regarded as stationary targets which the small ions approach normally from all directions with a velocity equal to the radial component of their Brownian velocity. Divergence of the small ions from the normal path owing to attraction by small ions of opposite sign may be neglected when nuclei are numerous, since in these circumstances the frequency of recombination with small ions of opposite sign is negligible compared with the frequency of recombination with nuclei.

If the ions and the nuclei were merely geometrical points we could say that the number of small ions crossing the boundary of a sphere of radius R in time t is equal to $4\pi R^2 n_1 v t$, where v is the average radial component of their velocity. Of these half enter and half leave the sphere, so the number entering the sphere is $2\pi R^2 n_1 v t$. Of these a certain proportion have been inside the sphere previously, but if R is not large compared with the mean free path that proportion must be small. *We make the assumption that the proportion is negligible when R is put equal to r, the radius of an uncharged nucleus* and deduce that the probable number of ions colliding with the nucleus in time t is $2\pi r^2 n_1 v t$. Further, since the average value of the cosine of the angle which the line of approach makes with the radius of nucleus is $\frac{1}{2}$, we have $v = \frac{1}{2}U$, where U is the mean velocity of the ions. Hence the number of collisions in unit volume and in unit time is $\pi r^2 n_1 U N_0$.

The frequency of recombination is by definition $\eta_{10} n_1 N_0$. Hence if each collision is followed by recombination we have

$$\eta_{10} = \pi r^2 U \qquad \ldots\ldots(1{\cdot}2).$$

It may be noticed that this is a limiting case of Harper's formula for η_{10}.

Formula (1·2) is different from that given in my earlier paper[7], referred to above. In deriving the earlier formula, which is erroneous, the fact was overlooked that the number of small ions colliding with an uncharged nucleus is only one-half of the number crossing the boundary of a sphere equal in size to the nucleus. Moreover, the value of v was taken to be the root of mean square of the radial component instead of the average value. According to the new formula the values of the radius of the nuclei given in my earlier paper would be increased by about 50 per cent.

§ 5. THE VALUE OF U

If the distribution of velocity amongst the small ions is Maxwellian then

$$U = \sqrt{\frac{8}{3\pi}} . C \qquad \ldots\ldots(5{\cdot}1),$$

C where C is the root of mean square or standard velocity. If a small ion consists of n' a cluster of n' molecules of water vapour, each of mass m, then

$$\tfrac{1}{2} n' m C^2 = 3R\theta/2N' \qquad \ldots\ldots(5{\cdot}2),$$

R, θ where R is the gas constant, $8{\cdot}32 \times 10^7$ ergs per gram-molecule, θ is the absolute N' temperature (say 283 degrees in the present case), and N' is Avogadro's number.

Accordingly

$$U^2 = \frac{8}{\pi} \frac{R\theta}{N' n' m} \qquad \ldots\ldots(5{\cdot}3).$$

Remembering that the mass of one molecule of water vapour is $18/N'$ we find that

$$U = 10^4 \times \sqrt{\frac{33}{n'}} \qquad \ldots\ldots(5{\cdot}4).$$

It is usually considered[8,9] that the number of molecules* in a small ion cluster is about 10 or 12. Taking $n' = 11$, we have

$$U = 1{\cdot}73 \times 10^4 \text{ cm./sec.} \qquad \ldots\ldots(5{\cdot}5).$$

* Loeb, discussing the cluster theory of the formation of small ions[9] shows that a monomolecular layer cluster would be stable. He goes on to say, "Were the nucleus and molecules spheres of the same size the maximum number of molecules in a stable cluster would be 12. A cluster of more than 12 molecules would require another layer, for 12 molecules is all that can be placed round a sphere of the same size". He then shows that if there were another layer of molecules the cluster would be unstable, for the kinetic energy of agitation would be greater than the potential energy, and so the molecules would not be bound in a closed orbit. Finally "it is very unlikely that the ion cluster numbers more than 12 molecules".

§6. THE VALUES OF r

With this value of U the formula (1·2) becomes

$$\eta_{10} = 5{\cdot}45 \times 10^4 r^2 \qquad \text{.....(6·1).}$$

Values of r deduced from those of η_{10} by means of equation (6·1) are shown in table 1 and are plotted in figure 2 against the values of the relative humidity with

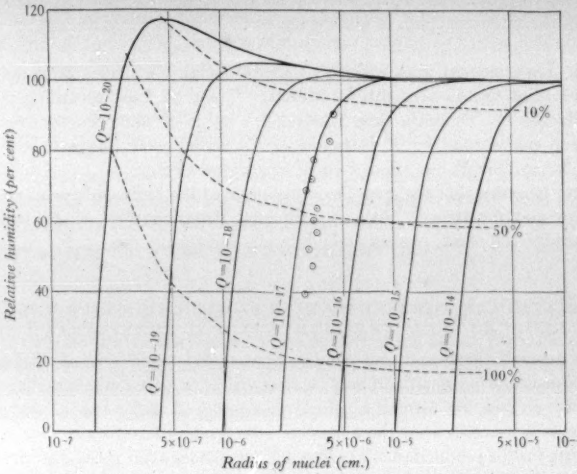

Figure 2. Variation in the radius of nuclei with relative humidity. The full lines represent the equation $H/100 = \exp\{P/r\} - Qr^3$ for $P = 11{\cdot}8 \times 10^{-8}$ and various values of Q. The broken lines represent the equation $c/100 = 1{\cdot}2\ Q/r^3$. ⊙ denotes values at Kew Observatory at 15h.

which they are associated. It will be observed that the changes in r are but slight until the relative humidity attains a value equal to about 80 per cent, conforming with the statement frequently made that condensation on nuclei commences when the relative humidity reaches about 80 per cent. Since it is evident on physical grounds that condensation will commence whenever there is an increase in relative humidity, it would be more strictly correct to say that the effect of condensation begins to be appreciable when the relative humidity reaches about 80 per cent.

The form of the variation in r with relative humidity, as shown by the plotted points, approximates closely to that of the family of curves drawn in the diagram. These curves may be obtained from theoretical considerations as will be shown below.

§7. COMPARISON WITH VALUES OBTAINED BY OTHER METHODS

The values which we have obtained for the radius of the nuclei are of the same order of magnitude as that given by Thomson[10] for the radius of the large ion, generally supposed to be identical with a charged nucleus. From con-

siderations of the motion of an electrified sphere through a viscous gas, by a method due to Cunningham[11], Thomson gives the following formula relating the mobility K of the large ion to its radius r

K, r

$$K = \frac{e\,(1 + 3l/2r)}{6\pi\mu r},$$

μ, l where μ is the coefficient of viscosity of the gas ($1{\cdot}83 \times 10^{-4}$ for air) and l is the length of the mean free path of a molecule of the gas (10^{-5} cm. for air).

There is some doubt as to the value of the coefficient of l/r to be used in this formula. Experimental work indicates that the factor 3/2 should be replaced by 0·864 according to measurements by Millikan[12], and by unity according to those by McKeehan[13]. Thomson uses McKeehan's value of unity for the coefficient of l/r, and substituting for K the value of the mobility of Langevin ions, viz., 1/3000 cm./sec. per V./cm., finds r equal to $4{\cdot}5 \times 10^{-6}$ cm.

It may be noted that the most recent estimate of the radius of nuclei, deduced by Nolan and Guerrini[14] from experimental determinations of the diffusion coefficients of the nuclei present in Dublin air, is $2{\cdot}85 \times 10^{-6}$ cm.

§ 8. VARIATION IN THE SIZE OF NUCLEI WITH RELATIVE HUMIDITY AS DEDUCED FROM THERMODYNAMICAL CONSIDERATIONS

It is generally supposed that condensation nuclei, which are of ultra-microscopic dimensions in dry air and only become visible in saturated air in the form of fog, cloud, or rain, are formed by the condensation of water vapour on suitable hygroscopic substances when these happen to be produced in the air. One possible mechanism for the production of hygroscopic substances in air is the distintegration of sea spray by the action of wind on the surface of the sea; in this case the hygroscopic substance in the resulting nuclei would be one or more of the hygroscopic salts contained in sea-water. Another possible mechanism is indicated by some recent experiments by J. H. Coste and the present writer[15] which were made in order to examine the constitution of the nuclei formed in the process of combustion, as it has long been known that copious formation of nuclei follows the combustion of any kind of fuel. These experiments suggest that the nuclei so produced are solutions of nitrous acid formed by the union of atmospheric oxygen and nitrogen at the high temperatures occurring in the neighbourhood of the flame, and their subsequent combination with water vapour. Nitrous acid is however unstable and it is probable that collisions between nitrous acid nuclei and molecules of sulphur dioxide gas, evolved when fuel is burned, result in the oxidation of the sulphur dioxide by nitrous acid to form trioxide, with the liberation of gaseous nitrous acid or oxides of nitrogen, the trioxide uniting with water to form sulphuric acid. Hence of the nuclei produced by combustion some may be nitrous acid and some sulphuric acid.

The newly formed hygroscopic droplets abstract molecules of water from the air until an equilibrium state is reached in which the pressure of water vapour at the surface of the droplet is equal to that of the vapour of the air. Any subsequent

disturbance of the equilibrium state by an external influence, such as a change in temperature due to radiation, convection, or conduction, leads to inequality between the two vapour pressures and inaugurates a process either of condensation or of evaporation whereby molecules of water are exchanged between the droplet and the air until another stable state is reached.

Thus the equilibrium size of a droplet depends upon the amount of water vapour in the air, and the condition for equilibrium is equality between the vapour pressure at the surface of the droplet and that of the water vapour in the air. This condition may be expressed mathematically as follows.

§ 9. THE HUMIDITY EQUATION

The vapour pressure over the surface of a spherical droplet is greater than that over a plane surface owing to the effect of surface tension. It has been shown by Kelvin[6] that if p denotes the vapour pressure over a plane surface of water and p' that over a spherical droplet at the same temperature

p p'

$$\frac{p'}{p} = \exp \frac{2T}{\sigma R \theta r} \qquad \text{.....(9·1),}$$

where T denotes the surface tension, σ the density of the liquid, R the gas constant for the vapour, θ the temperature of the droplet, and r the radius of the droplet.

T, σ, R θ, r

In the case of a solution, however, the vapour pressure at the surface is less than that over pure water by an amount δp, where

$$\frac{\delta p}{p} = CM \qquad \text{.....(9·2),}$$

M denoting the number of gram-molecules of solute per 1000 g. of solution and C a quantity which depends on the nature of the solute and for a given solute varies slightly with the concentration. Values of C for a great many substances are to be found in the *International Critical Tables*, **3**, 292. Average values of C for those

M, C

Table 2. Molecular weights and hygroscopic factors for various substances

Chemical formula	$MgCl_2$	NaCl	HNO_2	H_2SO_4
Molecular weight w	95	58	47	98
Hygroscopic factor C	8×10^{-2}	4×10^{-2}	(4×10^{-2})	4×10^{-2}
m/Q or $\pi\sigma w/750\, C$	5	6	(5)	10

substances of which atmospheric nuclei seem most likely to be constituted are shown in table 2. The hygroscopic properties of nitrous acid are not known owing to its instability, but as it is very attractive to water, its hygroscopic properties may be supposed to be not greatly different from those of sulphuric acid. Accordingly the value of C for sulphuric acid may also be used provisionally for nitrous acid.

The quantity M is a function of the radius of the droplet since it depends on the concentration of the solution. If m denotes the mass of the solute contained

m

w in the nucleus, which for a given nucleus remains constant, and w denotes the molecular weight of the solute, then the mass of the solution being $\frac{4}{3}\pi r^3\sigma$, we have

$$M = 1000\frac{m/w}{\frac{4}{3}\pi r^3\sigma} = \frac{750m}{\pi r^3\sigma w}$$

and so equation (9·2) becomes

$$\frac{\delta p}{p} = \frac{750\,mC}{\pi r^3\sigma w} \qquad \ldots\ldots(9\cdot3).$$

Combining* equations (9·1) and (9·3) we have for the vapour pressure p' at the surface of a hygroscopic droplet

$$\frac{p'}{p} = \exp\left\{\frac{2T}{\sigma R\theta r}\right\} - \frac{750\,mC}{\pi r^3\sigma w} \qquad \ldots\ldots(9\cdot4).$$

e' If e' denotes the pressure of water vapour in the surrounding air, the condition for equilibrium is that

$$p' = e' \qquad \ldots\ldots(9\cdot5).$$

Assuming that the temperature of the droplet is the same as that of the surrounding air, p is equal to the vapour pressure over a plane surface of water at *air* temperature, and hence if H denotes the relative humidity, we have from the definition of relative humidity

H

$$\frac{H}{100} = \frac{e'}{p} \qquad \ldots\ldots(9\cdot6).$$

Equations (9·4), (9·5) and (9·6) give at once

$$\frac{H}{100} = \exp\left\{\frac{2T}{\sigma R\theta r}\right\} - \frac{750\,mC}{\pi r^3\sigma w},$$

which it is convenient to write in the form

P, Q

$$\frac{H}{100} = \exp\frac{P}{r} - \frac{Q}{r^3} \qquad \ldots\ldots(9\cdot7),$$

where

$$P = \frac{2T}{\sigma R\theta} \quad \text{and} \quad Q = \frac{750\,mC}{\pi\sigma w}.$$

This is the desired equation expressing the equilibrium condition between droplets and aqueous vapour, and when the values of P and Q are known the equation can be used to find the radius of nuclei in equilibrium with air of given relative humidity.

§ 10. GRAPHICAL REPRESENTATION

Since T, σ and R vary but slightly, the quantity P depends chiefly upon the temperature θ of the droplets. The temperature of droplets in the free air near the earth's surface may be subject to a diurnal variation of some 30° C., a variation of about 5 per cent from the mean, but by partial differentiation of equation (9·7) it is found that the error in the value of H due to an error of as much as 10 per cent

* It should be remarked that, as Bennett[17] has pointed out, it is open to question whether equation (9·2) is applicable to the case of small surfaces.

in P is only 2 per cent for very small droplets of radius 6×10^{-7} cm., and 1 per cent for droplets of radius 10^{-6} cm., and decreases rapidly for larger droplets. Thus relatively small changes in the temperature of nuclei such as those due to diurnal variation may be neglected, and an average value of P may be adopted. Taking $T = 74$ dyne/cm^2, $\sigma = 1$ g./cm^3, $R = (83{\cdot}15 \times 10^6/18)$ ergs, and $\theta = 283°$ K., the value of P is found to be $11{\cdot}3 \times 10^{-8}$. This value will be used throughout.

The quantity Q depends chiefly upon the mass of hygroscopic substance, when the nature of the substance is determined, that is, when w and C are known. The hygroscopic factor C may vary with the concentration of solution, particularly when the solution becomes very dilute and the phenomenon of dissociation occurs. As shown by the values of m/Q in table 2, which are calculated from those of w and C, the value of Q is roughly equal to one-fifth that of the mass of hygroscopic substance in the nucleus, except in the case of sulphuric-acid nuclei for which the value of Q is one-tenth that of m.

Since nothing is known as to the value of m we must consider Q as liable to extensive variation. By assigning in turn different values to Q, the variation of r with H given by equation (9·7) may be plotted in the form of an isopleth diagram. Figure 2 is such a diagram, the different values adopted for Q being 10^{-20}, $10^{-19} \ldots 10^{-14}$. Semi-logarithmic scales are used in the figure owing to the wide range in the values of r which have to be taken into account.

§ 11. THE CONCENTRATION OF SOLUTE IN THE NUCLEI

A rough estimate may be formed of the concentration of solute in the nuclei. If the concentration is c per cent we have, since the mass of the droplet is $\frac{4}{3}\pi r^3\sigma$,

$$\frac{c}{100} = \frac{m}{\frac{4}{3}\pi r^3\sigma} \simeq \frac{5Q}{\frac{4}{3}\pi r^3\sigma} = 1{\cdot}2\,\frac{Q}{r^3} \qquad \ldots\ldots(11{\cdot}1),$$

except for sulphuric acid for which the coefficient of Q has to be doubled. Isopleths of concentration equal to 10, 50 and 100 per cent have been constructed to represent this approximate formula and are shown by the broken lines in figure 2. For sulphuric-acid nuclei the values would be double those marked in the diagram, which apply to the other substances. It should be emphasized that the values of the concentration are only rough approximations and are intended to serve merely as a guide. No rigour can be claimed for inferences deduced from their use, and it is for this reason that the full curves in figure 2 have been continued beyond the broken curve denoting 100-per-cent concentration.

It may be noted here that the use of unity for the density of nuclei is strictly justified only when the concentration of solute is not excessive. The changes in the form of the isopleths due to changes in density are however slight and are not worth considering at this stage.

§ 12. THE CASE OF CHARGED NUCLEI

It will be remarked that we have not considered the influence on the size of the nuclei exerted by the alternating acquisition and loss of electric charge which they experience. The potential energy due to the presence of an electric charge on a

droplet reduces the vapour pressure at the surface, but it is readily seen that for droplets of nuclear dimensions this effect is ordinarily negligible.

As has been shown by Thomson[18], the effect of electric charge may be represented by the addition of a term in equation (9·1) which becomes

$$\frac{p}{p'} = \exp \frac{1}{\sigma R\theta} \left\{ \frac{2T}{r} - \frac{n^2 e^2}{8\pi r^2} \right\},$$

n, *e* where n denotes the number of elementary charges e carried by the nucleus. The ratio of the two terms within the brackets is, when the values of e and T are substituted, $61 \times 10^{-18}\, n^2/r^3$, and is less than 1 per cent in the case of singly charged nuclei ($n=1$) if $r > 2 \times 10^{-7}$ cm., and in the case of doubly charged nuclei ($n=2$) if $r > 3 \times 10^{-7}$ cm. The values found for the radius of the nuclei at Kew are considerably higher than these, and unless the nuclei are multiply charged the difference between the sizes of the charged and uncharged nuclei is negligibly small.

Multiply charged nuclei are rare, and although Scrase[19] has found that droplets in fog carry charges of $34e$ the radius of fog droplets is so large that the effect of even such a high charge is in these circumstances insignificant. It would appear then that the effect of electric charge on the equilibrium size of nuclei may normally be regarded as a second-order quantity, becoming appreciable only in the rare case of multiply charged intermediate ions.

§ 13. DISCUSSION OF THE ISOPLETH DIAGRAM

The curves drawn in figure 2 are essentially similar to those given by Köhler[1] showing how the vapour pressure at the surface of droplets, which contain known concentrations of salts, chiefly sodium chloride, and are at a temperature of 273°, varies with a quantity proportional to the logarithm of the volume of the droplet. The most remarkable feature of the family of curves is that each of them crosses the saturation line and then returns to it. This means that when supersaturation occurs, owing to the depression of the air-temperature below that of the dew point, water is deposited on the droplets which consequently increase in size and are eventually in equilibrium with air which is just saturated. Thus the presence of the nuclei prevents conditions of high supersaturation being attained and intensified. The final size of the droplets would appear to be determined by the number taking part in the process and by the depression of the temperature below the original dew-point temperature, since the presaturation size of the nuclei is usually negligible in comparison.

Another important phenomenon indicated by the curves is the restriction of the deposition of moisture under conditions of supersaturation to those nuclei for which Q is greatest. Less supersaturation is required for deposition to occur on these, indeed for large values of Q the supersaturation need only be trifling, and once the requisite degree of supersaturation is attained, the ensuing deposition of moisture upon nuclei in this group prevents the attainment of the higher supersaturation necessary for deposition to occur on the remaining nuclei. Bennett has remarked upon this, pointing out[17] that "the number of drops in a fog rarely

attains a value as high as 1500 per c.c., while the number of Aitken nuclei is usually ten times this figure". Since in dry air the nuclei for which Q is greatest are those of greatest size and therefore those which on acquiring electric charges would be the slowest ions, it appears that, unless Q changes appreciably as saturation is approached, deposition of moisture when supersaturation is reached would occur most readily on the large ions of lowest mobility.

The curves indicate that in dry air the growth of nuclei with relative humidity is slow until humidities of about 80 per cent or so are reached, and agree very well with the form of the variation inferred from the Kew observations, as the plotted points show.

§ 14. THE VALUES OF m

It may be seen from the diagram in figure 2 that the plotted points may be divided into two categories, one in which the relative humidity is greater than 66 per cent, the other in which the humidity is less than this figure. Since at 15 h., when Scrase's observations were made, high humidities are associated with the winter months and low humidities with the summer months, this indicates an annual variation in the value of Q. From the values of Q shown in table 1, which are calculated from those of r and H by use of formula (9·7), it may be seen that the value of Q associated with low humidities, that is in summer, is on the average 18×10^{-18}, while that associated with high humidities, that is in winter, is 12×10^{-18}.

There are two sources of variation in Q, one being C, the hygroscopic factor, and the other m, the mass of hygroscopic substance in the nucleus. Generally, C may be expected to increase rather than decrease as the concentration of solution diminishes; whereas inspection of the isopleths of concentration in figure 2 shows that the category of points for which the concentration is least (the higher humidities) corresponds with the lower value of Q. Thus it appears that the source of variation in Q is to be found in variations in m, and the calculations imply that the value of m is less in winter than in summer.

If the nuclei consist of a substance for which the value of m/Q is 5, as we have assumed for nitrous acid (see table 2), the mass of hygroscopic substance in each nucleus corresponding to the above values of Q is 90×10^{-18} g. in summer and 60×10^{-18} g. in winter. Since the average values of the concentration of nuclei at Kew at 15 h. are[20] 20,000 per cm.^{3} in summer and 38,000 per cm.^{3} in winter it follows that the total concentration of hygroscopic substance in the nuclei in 1 cm.^{3} of air is 18×10^{-13} g. in summer and 23×10^{-13} g. in winter. If the nuclei consist of sulphuric acid, these values must be doubled (see table 2).

The conclusion that there is a greater concentration of hygroscopic substance present in winter than in summer seems reasonable in view of the increased combustion in winter and also of the relative absence of the convection which tends to expel atmospheric pollution from the lower atmosphere.

The value of the concentration of sulphuric acid in nucleus form, viz., about

4×10^{-12} g. per cm.^{3}, may be compared with the concentration of sulphuric acid in London air found, in the course of work not yet published, by Coste and Courtier, who analysed the condensate obtained by cooling air, freed from acid gases, by passing it through a vessel surrounded with ice. The amounts of sulphuric acid found by them varied from 4 to 20×10^{-12} g. per cm.^{3}, the higher results being usually associated with fog and the lower ones with rain.

Similar figures for nitrous acid may be obtained from the determination, by Francis and Parsons[21], of the oxides of nitrogen in the air of St James's Square, London. They found from 0·3 to 16·8 parts per 100 million by volume, calculated as nitric oxide, equivalent to from 6 to 354×10^{-12} g. per cm.^{3} of nitrous acid.

It will be noticed that these values are considerably in excess of the values deduced for Kew. This may be because the experimental values were obtained in air in the centre of London while Kew is near the outskirts, some ten miles from the centre. In the case of the oxides of nitrogen a large proportion of these are in gaseous form, and as the experimental results refer to the total concentration, gaseous and liquid, the amount of nitrous acid existing in liquid form as condensation nuclei must be much less than the total concentration found from the experiments.

§ 15. CONCLUSION

It should be pointed out that our treatment of the Kew observations does not take into account the possibility of the nuclei being heterogeneous. Thus the results should be considered as the average for various types of nuclei, if these in fact exist at Kew. It seems likely however that at Kew, fire-produced nuclei form a highly predominating group, and if this is the case it is a legitimate approximation to treat the nuclei as belonging to a single group. Further work along these lines may be expected to show the degree of accuracy of the approximation.

It appears from the foregoing analysis that, since P is not appreciably variable, the value of Q is the factor which determines the size of nuclei under prescribed humidity conditions in non-saturated air. Determination of the values of Q at different places and at different times of year provides a subject for further research which can hardly fail to yield information on the difficult problem of the origin and nature of hygroscopic nuclei.

§ 16. ACKNOWLEDGMENTS

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THE EFFECT OF AN ACOUSTICALLY ABSORBENT LINING UPON THE SOUND-INSULATING VALUE OF A DOUBLE PARTITION

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ABSTRACT. A study is made of the effect of rendering the interior of double partitions acoustically absorbent. A formula is derived for the effect of the treatment and is confirmed by measurements made upon double partitions containing various amounts of absorbent. The measurements show that considerable increases in the sound-insulation of a double partition can be obtained by the judicious use of it. In particular, in the case of a double window, an increase of some 8 db. can be obtained by covering with absorbent the wall surfaces enclosed between the two panes of glass.

§ 1. INTRODUCTION

Measurements made at the National Physical Laboratory and elsewhere have shown that the average sound-insulating effect of a single partition, e.g. a sheet of glass or a brick wall, is determined almost entirely by its weight per square foot. Consequently, high sound-insulation is only obtainable by making such partitions heavy. In many partitions this is undesirable, for instance a glass window; in others it is impracticable, for instance the wall of an aeroplane cabin or a partition in a modern multi-storey building. In such cases recourse is had to multiple partitions, double windows, double aluminium panels and double building-block partitions respectively being used.

In an earlier paper[1] the author has shown that the sound-insulating value of a light air-spaced double partition, in which the sole coupling between the components is the air in the interspace, is dependent upon the thickness of the spacing. It is the purpose of the present paper to describe how the sound-insulating value of such a partition may be increased by suitably disposing acoustical absorbent material within it.

§ 2. THEORETICAL CONSIDERATIONS

The calculations given below do not pretend to be exact, but serve to show the mechanism by which the absorbent interior of a double partition affects its sound-insulating qualities. It will appear later, however, that the formula obtained gives results which are in reasonable agreement with experiment.

Figure 1 represents an air-spaced double partition situated between two acoustically dead rooms, so that sound returned to the partition from the side remote from the sound source need not be considered.* The fixing of the two sheets is taken to be such that the energy transferred from one sheet to the other *via* the edges can be neglected.

The sound-reduction factor of the partition will, of course, vary with the angle of incidence of the sound, but if the sound-reduction is first calculated for a ray having a particular angle of incidence, the result can be generalized for all angles of incidence by using mean values for the sound-reduction factors and absorption coefficients of the constituents of the partitions.

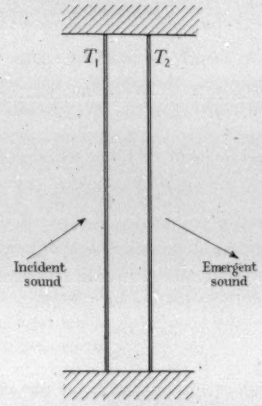

Figure 1.

Let the sound-reduction factors of the transmitting panels T_1 and T_2 be R_1 and R_2 respectively for the particular angles of incidence considered. R_1 R_2

If sound of energy dE, being part of a ray of sound travelling in the direction of the arrow, falls upon the partition during time dt, it will be divided into two parts by T_1—a transmitted part of energy dE/R_1 and a reflected part of energy $dE\,(1-1/R_1)$. The transmitted sound will be reflected backwards and forwards between the interior surfaces of the partition and some of the reflections will take place at the transmitting panels T_1 and T_2. At each incidence upon the two transmitting surfaces average fractions $1/R_1$ and $1/R_2$ respectively of the energy of the sound will be transmitted out of the partition. There will be a certain average circuit which the sound traverses between successive incidences upon T_2. In this circuit dE dt

* This restriction, while simplifying the problem, does not render the conclusions less general, since the only effect of making the rooms reverberant would be to pass some sound back through the partition into the source room by an amount which can be allowed for by means of the ordinary theory of coupled rooms.

the sound visits the other surfaces and by absorption and transmission is reduced
m to a fraction $1/m$, say, of its value at the previous reflection.

Now such a ray may be considered as a stream of elements of energy such as the above. Let the ray have been incident upon the partition for a sufficient time for equilibrium to have become established. Then, assuming that sound passing through T_1 proceeds directly to T_2 and does not suffer a reflection at the margins on the way,* during any time interval dt there will be incident upon T_2 elements of energy which have travelled directly and others which have made one, two or more circuits. The former have energy dE/R_1, the others dE/mR_1, dE/m^2R_1 etc.

Thus the total energy falling upon T_2 in time dt due to the ray will be

$$\frac{dE}{R_1}\left(1+\frac{1}{m}+\frac{1}{m^2}+\text{etc.}\right)=\frac{mdE}{R_1(m-1)}.$$

Thus of the energy dE which is incident upon the partition, a fraction $mdE/\{R_1R_2(m-1)\}$ is transmitted through T_2. The reduction of sound by the partition as far as the particular ray we are considering is concerned is thus $R_1R_2(m-1)/m$.

Taking the average of all incident rays, the sound-reduction factor will be

$$\bar{R}_1\bar{R}_2(1-1/\bar{m}) \qquad \text{.....(1)},$$

$\bar{R}_1$, $\bar{R}_2$ where $\bar{R}_1$ and $\bar{R}_2$ are the sound-reduction factors of the two leaves T_1 and T_2
$\bar{m}$ averaged over all angles, and $\bar{m}$ is the mean value of m for all such angles.

Thus the effect of changing the absorbent character of the interior of the partition is to change its sound-reduction by a factor

$$\frac{1-1/\bar{m}'}{1-1/\bar{m}''} \qquad \text{.....(2)},$$

$\bar{m}'$, $\bar{m}''$ where $\bar{m}'$ and $\bar{m}''$ are the values appropriate to the two conditions.

We see from equation (1) that the reduction can never be greater than R_1R_2.

A word of caution is called for here, namely that R_1 and R_2 are the sound-reductions of T_1 and T_2 not when considered by themselves but when combined in the form of the double partition. This warning is necessary since, as shown in a previous paper[1], two sheets such as we are considering react upon each other through the elasticity of the separating air and acquire new resonant frequencies in addition to those they would possess by themselves. It thus happens that their effective sound-reduction may be lower when combined than when taken separately.

§ 3. CALCULATION OF $\bar{m}$

Let the areas of the transmitting faces T_1 and T_2 be A_1 and A_2 and the areas of
$A_1 \ldots A_6$ the other four interior surfaces be A_3, A_4, A_5 and A_6. Let the absorption coeffi-
$\alpha_1 \ldots \alpha_6$ cients of the six surfaces be α_1, α_2, α_3, α_4, α_5, α_6, averaged over all angles of incidence.

* In view of the usual proportions of this type of partition, this must be true of the greater part of the sound.

Then in any given time-interval the sound will be reflected at each of the surfaces a number of times proportional to its area. Thus for each reflection at T_2 (by which the sound leaves the partition) there will be A_1/A_2 reflections at T_1, A_3/A_2 reflections at surface (3), and so on.

At each reflection at T_1 the sound loses, by absorption and transmission, an average fraction $(\alpha_1 + 1/R_1)$, and a similar expression holds for T_2. At each reflection at the other surfaces, which are assumed not to transmit appreciably, it will lose fractions α_3, α_4, α_5 and α_6 respectively.

Thus in the complete circuit the sound is reduced on an average to a fraction $1/m$ such that

$$\frac{1}{m} = \left(1-\alpha_1-\frac{1}{R_1}\right)^{A_1/A_2}\left(1-\alpha_2-\frac{1}{R_2}\right)(1-\alpha_3)^{A_3/A_2}(1-\alpha_4)^{A_4/A_2}(1-\alpha_5)^{A_5/A_2}(1-\alpha_6)^{A_6/A_2} \qquad \ldots\ldots(3),$$

which is the result required.

It may be noted that this formula expresses what was implied in the method of derivation: provided that the areas are the same, the absorbent is equally effective whether placed on the leaves of the partition or on the side walls. If, as in the usual partition, the areas of the transmitting surfaces are equal to A, and the interior surfaces of the sides of the partition all have the same absorption coefficient α, equation (3) becomes

$$\frac{1}{m} = \left(1-\alpha_1-\frac{1}{R_1}\right)\left(1-\alpha_2-\frac{1}{R_2}\right)(1-\alpha)^{\frac{S}{A}} \qquad \ldots\ldots(4),$$

where $$s = A_3 + A_4 + A_5 + A_6.$$

Thus, by combining equation (4) with equation (1), we have that the sound-reduction R due to such a partition will be given by

$$R = R_1 R_2\left(1-\left[\left(1-\alpha_1-\frac{1}{R_2}\right)\left(1-\alpha_2-\frac{1}{R_2}\right)(1-\alpha)^{\frac{S}{A}}\right]\right) \qquad \ldots\ldots(5).$$

When the absorption coefficients are small equation (5) takes the simple form

$$R = \frac{R_1 R_2}{A_2} \times (\text{total absorbing power of the interspace}),$$

the total absorbing power including, of course, the losses due to transmission through the panels.

By taking logarithms of both sides of equation (3) we obtain

$$A_2 \log_e\left(\frac{1}{m}\right) = A_1 \log_e\left(1-\alpha_1-\frac{1}{R_1}\right) + A_2 \log_e\left(1-\alpha_2-\frac{1}{R_2}\right) + \sum_3^6 A_r \log_e(1-\alpha_r).$$

The expression on the right bears an obvious resemblance to the denominator in G. Millington's formula for the reverberation period of a room[2], viz.:

$$T = \frac{0{\cdot}05V}{-\Sigma A_1 \log_e(1-\alpha_1)},$$

where T is the reverberation period and V the volume. This is a consequence of the use of Millington's method of calculating the effect of the absorbent.

§ 4. EXPERIMENTAL RESULTS

The above calculations show that the introduction of absorbent into the interior of a partition should, when the interior is initially reverberant, considerably increase its sound-insulation. To test this and to compare the amount of the increase with that predicted by equation (5), an air-spaced double partition 2 ft. 6 in. square was built.

Light aluminium sheets weighing 0·3 lb. per square foot were used, since experience had shown that coupling between the edges is small in this type of partition. In order that a wide range of absorption coefficients for the interior surfaces might be used, special care was taken to commence with a highly reverberant interior. For this purpose the partition was formed by fixing the two aluminium sheets in an aperture in a steel diaphragm 9 in. thick. The side walls of the partition were thus of heavy steel. The diaphragm was mounted in the test aperture between the large sound-transmission rooms at the National Physical Laboratory. Two separations of the sheets were experimented with, namely 8 in. and 4 in.

Arrangements were made for supporting sheets of absorbent material against the steel interior surfaces of the partition. This position was chosen because if the absorbent had been hung against the aluminium sheets their mass and hence their sound-reduction would have been affected. Two absorbents were tried in the 8-in. partition, one an acoustic felt with an absorption coefficient of about 0·6 and the other a fibre board with an absorption coefficient of about 0·2. The acoustic felt only was tried in the 4-in. partition.

Measurements of the sound-reduction factor of the double partition were made both with and without the absorbent in position. Measurements were also made of the sound-reduction factor of one of the sheets of aluminium alone. The measurement rooms were used in a reverberant condition so that sound was incident at all angles upon the partition, and to minimize stationary wave effects, a warble test note was used, the note varying periodically in frequency by 10 per cent of its mean value. The following were the mean frequencies used for the measurements: 200, 400, 800, 1000 and 2000 cycles per second.

In each case an increase in the sound insulation was observed when the interior of the partition was rendered absorbent. The results obtained are given in table 1 below, in which are also given, for comparison, the values calculated from equations (2) and (3). It will be seen that the agreement is fairly good.

For the calculated values it is necessary to assume some value for the absorption coefficients of the aluminium and steel surfaces. A reasonable estimate can be formed for the steel surface since it was painted and was thus very similar to painted hard plaster, the absorption coefficient of which has been measured at the laboratory and found to be about 0·015. A figure for the absorption coefficient of the aluminium surface is more difficult to estimate. Measurements made by Davis and Evans[3] by the stationary-wave method have indicated that a metal surface may absorb

between 0·2 and 1 per cent of the energy of a wave incident normally. An empirical relation obtained by these authors shows that the absorption coefficient for reverberant sound (such as was used for the transmission measurements above described)

Table 1. Comparison of calculated and observed increases in sound-reduction caused by rendering absorbent the interior of a double partition made of aluminium weighing 0·3 lb./ft.^{2}

Frequency (c./sec.)	Thickness of partition 8 in.				Thickness of partition 4 in.	
	Increase due to absorbent felt		Increase due to fibre board		Increase due to absorbent felt	
	Calculated	Observed	Calculated	Observed	Calculated	Observed
	db.	db.	db.	db.	db.	db.
2000	13	11	7·5	6	11	10
1000	12	9	6	5	9·5	10
800	11	7	5·5	2	8·5	5
400	6	4	3·5	0	4·5	3
200	3	4	2	0	1·5	2·5

would be considerably larger. It is not likely, however, that it would be larger than the figure for painted steelwork. A figure of 1 per cent was accordingly chosen for calculating the results shown in table 1. The values used for the absorption coefficients of the fibre board and absorbent felts and the sound-reduction factor of a single sheet of aluminium are given in table 2.

Table 2

Frequency (c./sec.)	Sound-reduction due to single sheet of aluminium (db.)	Absorption coefficient of absorbent felt	Absorption coefficient of fibre board
2000	27	0·7	0·2
1000	22	0·8	0·2
800	20	0·7	0·2
400	15	0·4	0·2
200	8	0·4	0·2

The absorption coefficients used were based upon Eyring's formula although coefficients based upon Millington's formula would have been in better accord with the method of derivation of equation (3). These coefficients were not obtainable, but the small differences between the coefficients obtained from the two formulae are not likely to have an appreciable effect upon the results given below.

The sound-reduction factor of a single sheet should have been obtained while the sheet actually formed part of the double partition. There does not seem to be any way of obtaining this figure, however, except by using equation (3) above. Accordingly the figure obtained from one sheet alone was used. As $1/R_1$ and $1/R_2$ are at most frequencies small compared with α_1 and α_2, and in any case the spacings

used were wide so that coupling effects would not be large, it is likely that the error thereby introduced is not serious.

Whilst the agreement between the measured and calculated values is fairly good, the calculated figures are, on the whole, somewhat larger than the observed. It would be possible to obtain better agreement by somewhat increasing the assumed values of the absorption coefficients for aluminium, but in the absence of reliable figures for these coefficients it is really not possible to say more than that formula (1) is capable of predicting the effect of an absorbent lining to a fair approximation but that there is no evidence to show whether it can be regarded as exact.

A more reliable check on the formula is obtainable by comparing the 8-in. partition lined with fibre board with the same partition lined with absorbent felt, for the absorption by the aluminium surfaces is then of no account. Assuming the same values for the absorption coefficients as before the results given below in table 3 are then obtainable.

Table 3. Increase in sound-insulation caused by substituting an absorbent felt lining for a lining of fibre board in a double aluminium partition.

Frequency (c./sec.)	Increase in sound insulation (db.)	
	Calculated	Observed
2000	5·5	5
1000	6	4
800	5·5	5
400	2·5	4
200	1	4

It will be seen that, allowing for the errors of measurement, which increase as the wave-length increases, there is reasonable agreement.

The conditions under which the experiments described above were made are, of course, exceptional and it is not likely, for instance, that a metal lining to a double window would occur in practice. However, surfaces of brick, plaster, painted plaster, or cement do very frequently occur in the interior of double partitions, for instance double windows. The absorption coefficient of the last-mentioned three surfaces is not likely to exceed 2 per cent, and hence the interior of any partition in which they occur may be highly reverberant as in the above experiments.

Bare brickwork is however more absorbent and it was therefore desirable to determine whether in this case also absorbent treatment would be advantageous. A set of measurements was therefore made in another pair of experimental rooms, in which the aperture has a bare brick surface. A double partition measuring approximately 5 by 4 ft. was formed from two sheets of iron sealed into the aperture at about $8\frac{1}{2}$ in. apart. The iron weighed 21 oz. per square foot and thus the partition corresponded closely with a double window of 21-oz. glass.

The measurements of the sound-transmission through the partition were made with a technique differing in some respects from that used for the aluminium partition described previously. A beam of sound incident obliquely upon the partition

was used and the note used was a pure tone, instead of a warble tone. The table below gives the increase in sound-reduction observed when the brickwork inside the partition was covered with absorbent felt having the absorption coefficients given in table 2. For comparison, the increase in sound-reduction calculated from equation (5) by the use of the absorption coefficients given for bare brickwork by W. C. Sabine and on the assumption that the iron has an absorption coefficient of 0·01 are also tabulated.

Table 4. Increase in the sound-insulating effect of a double sheet iron partition resulting from lining with absorbent felt the brick frame in which it was built. Weight of iron, 21 oz./ft.^{2}

Frequency (c./sec.)	Sound-reduction factor of single sheet (db.)	Absorption coefficient of bare brickwork (W. C. Sabine)	Absorption coefficient of felt	Increase in insulation due to absorbent lining (db.)	
				Observed	Calculated
2000	37	0·049	0·7	13	11
1000	32	0·042	0·8	10	10·5
500	22	0·031	0·7	3	10
300	18	0·025	0·4	7	5·5
200	17	0·024	0·4	5·5	5

Owing to the use of a pure tone these measurements are subject to a greater uncertainty than those detailed in table 1. It will be seen that there is a definite gain when the brickwork is covered with absorbent and that quite satisfactory agreement between the calculated and observed figures is obtained. As a matter of fact equally good agreement is obtained if the iron sheets are assumed not to be absorbent.

§ 5. CONCLUSION

The results described above have practical significance since they indicate that by the use of absorbent treatment a double partition can be given a greater sound-insulating value, or alternatively that the same sound-insulation can be obtained by using a double partition of lighter construction, provided it is lined with absorbent. Thus double windows, as usually built with bare or plastered brickwork exposed between the two components, could always be considerably improved by covering the brickwork with absorbent. Similarly, to obtain the greatest effect from light double aluminium partitions such as are used in aeroplane construction, the interior surfaces of the aluminium should be covered with absorbent material. This, incidentally, would have the additional advantage of reducing noise due to drumming. It is evident, however, that the absorbent treatment should not completely fill the space between the two leaves of the partition, for this would tend to provide a mechanical coupling between the two components of the partition and thus to defeat the object for which it was inserted.

The experiments also suggest that double brick partitions would be improved by an absorbent lining. It is, in fact, quite a common practice to hang an absorbent blanket between the two leaves of such a partition. Experiments are in progress to test whether there is any advantage in this procedure. Other experiments have shown, however, that in such partitions the coupling between the two members is largely mechanical and takes place through the edges, whereas in the light partitions studied above the coupling takes place through the air between the members. Hence any effect due to an absorbent lining is likely to be small.

§ 6. ACKNOWLEDGMENTS

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THE DENSITY AND COEFFICIENT OF EXPANSION OF LIQUID GALLIUM OVER A WIDE RANGE OF TEMPERATURE

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ABSTRACT. Accurate measurements of the density and coefficient of expansion of liquid gallium at temperatures from 30° to 1000° C. have been made by a dilatometric method. The temperature was measured with a platinum resistance thermometer. An equation expressing the increase in volume as a function of the temperature has been found, and from that equation values have been calculated for the coefficient of expansion.

§ 1. INTRODUCTION

The element gallium, occurring in group 3 of the periodic system, has a melting-point of 29·8° C., and an unknown boiling-point greater than 1600° C.* In recent years, Andrade has developed a theory of the viscosity of liquids[1], and in connexion with this theory an accurate measurement of the kinematic viscosity of gallium from 30° to 1100° C. has been made by K. E. Spells[2] in this laboratory. Liquid gallium was chosen because of the big range of temperature over which it can be used. In order to calculate the actual viscosity it is necessary to know the density of the liquid over this temperature-range. Further, the variation of density with temperature of an elementary liquid over a wide range of temperature will clearly be of interest as soon as a satisfactory theory of liquids has been developed. The only previous density-determination for liquid gallium was obtained by Richards and Boyer[3], who carried out a research on the purification of the metal and measured the density of both the liquid and the solid at the melting-point, showing that the metal expands on solidifying.

The known chemical properties are that the metal readily oxidizes in air and is soluble in concentrated hydrochloric and nitric acids, forming two series of salts. It amalgamates with mercury and forms alloys with many metals. The oxide is non-volatile but is soluble in dilute hydrochloric acid with the formation of gallous and gallic chlorides, which have boiling-points of about 535° and 210° C. respectively.

* Although there is no value for this boiling-point in the standard tables, there is a value of 2300° C. in the 1935 edition of Kohlrausch's *Praktische Physik*, but no reference is given.

§ 2. SOME PRELIMINARY MEASUREMENTS

As gallium is expensive only 4 cm.³ were available, and a few preliminary measurements of the mean coefficient of expansion were made with a pyrex-glass weight thermometer. It was necessary to fill this weight thermometer by a vacuum method, since the usual method of filling is impracticable for a liquid with such a high boiling-point, and the apparatus shown in figure 1 was made for this purpose. The weight thermometer *A*, made to hold about 2½ cm.³, was fitted with a ground joint, so that it could be detached from the rest of the apparatus, and it was first calibrated with mercury.

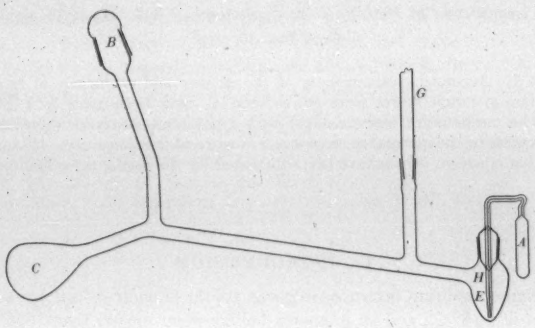

Figure 1.

The gallium was melted under dilute hydrochloric acid in a beaker and was poured into the bulb *C* through the opening *B*. The apparatus was evacuated through the tube *G*, when the remaining hydrochloric acid vaporized and was absorbed by solid potassium hydroxide. The gallium was then strongly heated to about 500° or 550° C., when the two chlorides volatilized and were deposited on the cool parts of the glass, leaving the gallium in a pure state. The metal then had the bright appearance of a globule of mercury, and flowed freely about the bulb *C*. This method of preparing gallium in a suitable condition was used by Spells[2] and also, with a slight difference, by Boyer[4]. The thin film of chloride formed in the first instance by the hydrochloric acid protects the metal from oxidation during its transfer to the apparatus. The gallium in the bulb *C* was then tipped into the bulb *E* and gas was let in through the tube *G*, so that the gallium was forced up the capillary tube *H* into the bulb *A*. The gas used was specially pure hydrogen, which had been found to have no effect on gallium in the cold. The weight thermometer was now removed from the apparatus and a few readings were taken in the usual way by heating to a definite temperature and weighing.

The values obtained for the mean coefficient of expansion α (corrected to the temperature-range 32·38° to 310° C.), and for the density of the liquid at the

melting-point, are given later. A few readings taken at 100° C. showed that the mean coefficient of expansion decreased with rise of temperature, the initial temperature being kept constant, but it was not possible to obtain accurate results over the smaller range as the weight of gallium expelled was small.

§ 3. THE DILATOMETRIC METHOD

In the experiments with the weight thermometer the method of filling was satisfactory, but with the measurements difficulty had been experienced owing to oxidation of the metal when it came into contact with air; hence a dilatometric method was adopted.

A quartz dilatometer in the form of a bulb and capillary tube was filled with gallium *in vacuo* and was heated in an electric furnace, the increase in height of the gallium meniscus being carefully measured. The dilatometer was calibrated with mercury. Three dilatometers were made for different temperature-ranges and the preliminary values obtained for the mean coefficient of expansion made it possible to calculate suitable values for their sizes.

The apparatus designed for filling the dilatometers is shown in figure 2. It was fitted on a board which could be turned about an axis through *C*. The portion of the apparatus beneath the joints *A* and *G* was made in quartz, whilst the upper portion was made in glass. The portion between the joints *A* and *B* was detachable and was made in triplicate with bulbs of different sizes at *D*. The dilatometer itself consisted of this bulb *D* together with the capillary tubes above and below, and would be sealed off at the points *E* and *F*. Five fine marks were made at equal intervals of 4 cm. on the capillary tube between *D* and *F*.

The tubes *H* and *J* were connected by short pieces of pressure tube to two vacuum systems. Tube *J* was connected to a Hyvac pump through tubes containing potassium hydroxide, phosphorus pentoxide, and calcium chloride: pure hydrogen could be admitted into this system. The tube *H* was connected to a two-stage mercury-vapour pump, through a liquid-air trap of the type designed by Andrade[5]. The ends of the tubes *J* and *H*, and the ends of the fixed tubes leading to the vacuum systems, were brought near to the axis of rotation at *C*, so that the pieces of pressure tube were as short as possible. Two other short pieces of pressure tube, *U* and *V*, were included as shown to facilitate the fitting of the ground joint *A*.

The following experimental procedure was adopted for filling and sealing off the dilatometer. About 2 cm^3 of gallium were treated with hydrochloric acid and were placed in the bulb *N*; the apparatus was then evacuated. The gallium in the bulb *N* was heated to a bright red heat for about 45 min., so that the chlorides were driven off.* The gallium was then allowed to cool and was tipped into the bulb *O*, where it was again heated for about 15 min. This second heating was to remove any traces of chloride that the gallium might have picked up in passing from *N* to *O*. The two bulbs *D* and *S* and the capillary tubes between *F* and *Q* were thoroughly

* It is interesting to note that gallium is slightly volatile at this temperature (about 900° C.), and a very faint deposit of metallic gallium appeared on the hot parts of the bulb during the heating.

baked out by heating with a hand blow-pipe. The gallium was now tipped into the bulb *R* and the tap *L* was closed. A little hydrogen was then admitted through the tube *J* so that the gallium rose slowly up through the bulb *S* into the dilatometer bulb *D*, and finally entered the capillary tube above that bulb. Both the bulbs *S* and *D* were kept hot during the filling. The pressure was adjusted so that the gallium meniscus was a little way above the top of the bulb *D*, and then the dilatometer was sealed off at the points *E* and *F*. It will be noticed that during this filling and sealing off a high vacuum was maintained above the gallium in the dilatometer by the mercury-diffusion pump.

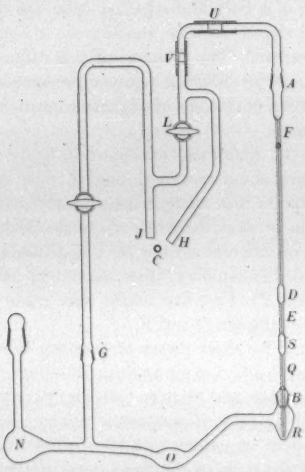

Figure 2.

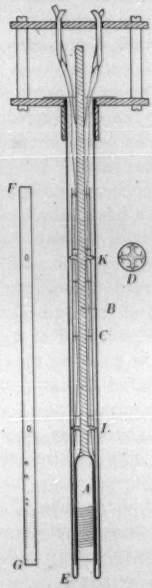

Figure 3.

The gallium dilatometer filled in this way was very satisfactory; when it was heated and cooled, the gallium showed no signs of sticking, and in appearance the gallium was indistinguishable from mercury. When calibrated, the dilatometer could be used as a high-temperature thermometer; such thermometers have also been made by Boyer[4]. Altogether three dilatometers were filled.

§ 4. MEASUREMENTS

For measuring the temperature a special platinum resistance thermometer, shown in figure 3, was constructed. The short quartz tube *A* was joined to a long quartz rod *B*, which had pieces of thinner quartz rod fixed to it in the form of two crosses *K* and *L*. Four mica strips, similar to the one *FG*, were fitted on to these crosses as shown in the section *D*. The thin platinum wire, which was specially pure, was carefully annealed and was wound in a spiral on the notches cut in the lower ends of the mica strips. The leads, which were of 22-gauge platinum wire, were kept in position by pieces of mica placed around the rod *B*; the compensating leads were joined by a short length of the wire used for the coil. A quartz tube *C* was slid over the assembled structure, and the two tubes *A* and *C* were sealed together at the bottom *E*. A brass head, waxed on to this outer tube at the top, held the flexible copper leads, which were soldered to the platinum leads. These flexible leads were connected to a Callendar and Griffiths bridge, and the thermometer was calibrated in ice, steam, and sulphur vapour. The constants found were as follows:

$$\frac{R_{100}}{R_0} = 1{\cdot}3905 \text{ and } \delta = 1{\cdot}50,$$

where R_0 and R_{100} are the resistances at 0° and 100° C. respectively, and δ is the usual correction factor. These values are in accordance with the standard specification[6].

The dilatometer and resistance thermometer were now heated together in an electric furnace. The resistance thermometer was used upside down, so that the end *E* projected vertically upwards into the furnace, and the bulb of the dilatometer then fitted into it so as to be surrounded by the coil of platinum wire. Copper filings were packed into the remaining space in the tube *A*. A close-fitting thick-walled copper tube, of about the same length as the quartz tube *A*, was slid over the end *E* of the resistance thermometer to prevent any temperature-gradient along the quartz.

In order to be able to read the position of the gallium meniscus in the capillary tube of the dilatometer and at the same time to heat the capillary tube as uniformly as possible, a subsidiary furnace was placed on the top of the main furnace. This subsidiary furnace was provided with two quartz windows, each about 2 cm. long and 0·7 cm. wide, through which a direct view of the stem of the dilatometer could be obtained. Readings were then taken as follows.

The two furnaces being at the required temperature, the height of the dilatometer was adjusted so that both the gallium meniscus and one of the marks on the stem of the dilatometer came into view through the window in the top furnace; such an adjustment was always possible, because the length of the window was 2 cm. and the distance between the marks on the dilatometer was 4 cm. The height of the gallium meniscus above or below the visible mark was then measured with a cathetometer. It was found impossible to keep the temperature perfectly constant, and a series of readings of temperature and meniscus was taken over a period of

about half an hour; these meniscus readings were then corrected to one temperature and their mean value was found. The mean heights thus obtained, together with the corresponding temperatures, are recorded in table 1; the heights are given as the total height above the initial mark. The negative sign indicates that the gallium meniscus was below this mark. The results for each dilatometer have been arranged in the order of increasing temperature, although actually they were taken in a random order; for instance, several of the points at other temperatures were taken between the two points at 235° C. The other columns of this table will be explained later.

Table 1

Dilatometer	Temperature (° C.)	Height (cm.)	Stem correction (cm.)	$\frac{V_2}{V_1}$
First	32·38	0·0108	—	1·00000
	299·92	5·2015	0·0567	1·03176
	346·45	6·0498	0·0661	1·03702
	427·53	7·5712	0·0378	1·04610
	476·94	8·4676	0·0492	1·05164
	571·76	10·1845	0·0364	1·06207
	651·71	11·5894	0·0365	1·07071
	732·17	13·0151	0·0412	1·07941
Second	32·38	− 1·2327	—	1·00000
	99·77	0·9349	0·0038	1·00834
	100·07	0·9470	0·000	1·00838
	160·25	2·8275	0·0009	1·01565
	190·81	3·7499	−0·0009	1·01923
	235·10	5·0689	−0·0023	1·02436
	235·37	5·0802	0·002	1·02440
	382·68	9·3088	0·0043	1·04114
Third	32·38	− 0·5057	—	1·00000
	685·71	8·9726	0·0106	1·07450
	880·69	11·5638	0·0192	1·09495
	1005·0	13·329	0·016	1·10876

In order that the results which were obtained with the different dilatometers might be compared, it was necessary to take a reading at some convenient reproducible low temperature near the melting-point of gallium, and the transition temperature of sodium sulphate, which is known to be 32·38° C., was chosen for this purpose. The first reading for each dilatometer was therefore taken at this temperature, the dilatometer being immersed directly in the melting salt. This reading was repeated after some of the readings at the higher temperatures had been taken, and the results showed that it remained unaltered.

With the two furnaces arranged as described, the temperature of the stem of the dilatometer was not uniform. This caused a small error in the observed height, and a correction for it was obtained as follows. If the temperature of the bulb of the dilatometer is $t_1°$, the temperature of any short length of the stem dl is $t_2°$, and the mean coefficient of expansion of gallium over the range $t_2°$ to $t_1°$ is α, then the correction to be added to the observed height is $\int \alpha\,(t_1 - t_2)\,dl$, the integral being taken from the level of the gallium meniscus down to the bulb, where the difference

in temperature becomes zero. This difference in temperature was measured with a thermocouple and a graph was plotted for each observation. The value of α can be assumed to be constant over the range of temperature involved in any one correction, and hence the value of the integral is easily obtained from the graph. The corrections obviously had to be obtained by successive approximation, and each correction is recorded under the heading "stem correction" in the fourth column of table 1. In the case of the first dilatometer the corrections are larger than in the cases of the other two, because the upper furnace was not used and hence there was a big temperature-gradient along the stem.

With the three dilatometers the complete range of temperatures from 100° to 1000° C. was covered. Readings with the first dilatometer were taken at temperatures from 300° to 730° C. The second dilatometer, which had a larger bulb, was used at temperatures between 100° and 380° C.: the points at 100° were taken with a hypsometer. The third dilatometer was designed for temperatures up to 1000° C.; with this one, however, only a few points were obtained, because the quartz devitrified at the high temperatures and it was then difficult to read accurately the height of the gallium meniscus. Owing to a slight defect in design, the resistance thermometer had to be rewound and recalibrated after the measurements with the first dilatometer.*

One remarkable property of gallium, which can conveniently be mentioned here and which was very noticeable during this work, is the great tendency of the metal to supercool. Two of the dilatometers were left at room-temperature for several months after the measurements had been taken, and the gallium still showed no signs of solidifying.

§ 5. CALIBRATION

The capillary tubes and the bulbs of the dilatometers were calibrated with mercury, and the distances between the reference marks on the capillary tubes were measured with a travelling microscope. The second and third dilatometers were calibrated before they were filled, but the first dilatometer was not calibrated until after the readings with it had been taken. A value for the density of gallium was obtained with the first dilatometer.

The capillary tube E, figure 2, was made so fine that any uncertainty as to its diameter at the point where it was sealed off produced a negligible error in the total volume of gallium.

§ 6. RESULTS

The results in the fifth column of table 1 are given as the ratio V_2/V_1, where V_1 is the volume of gallium at the initial temperature 32·38° C. and V_2 is the volume at a higher temperature t. Values for the coefficient of expansion of the quartz were taken from the tables.

By the method of least squares, the following equation has been found for the ratio V_2/V_1:

$$\frac{V_2}{V_1} = 0{\cdot}99587 + \frac{1}{10^6}(128{\cdot}40t - 0{\cdot}037801t^2 + 0{\cdot}00003401t^3 - 0{\cdot}000000001250t^4) \quad \ldots(1).$$

* The figures given on p. 704 are for the second calibration.

The coefficient of expansion, $V^{-1}\,dV/dt$, was calculated from the above equation, and values for it are plotted against temperature in figure 4. It is also possible to

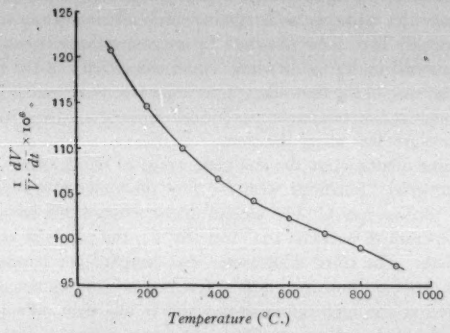

Figure 4.

calculate from equation (1) the mean coefficient of expansion between 32·38° and $t°$, defined by $(V_2 - V_1)/V_1\,(t - 32{\cdot}38)$; this has been done for $t = 310°$, and the value is compared below with the corresponding value obtained with the weight thermometer.

Coefficient of expansion calculated from equation (1) ... $118{\cdot}7 \times 10^{-6}$ per °C.
Weight-thermometer value ... ... $118{\cdot}4 \times 10^{-6}$ per °C.

The values obtained for the density* of gallium, corrected to 29·8° C., are as follows:

Density by weight thermometer	6·0946 g./ml.
Density by first dilatometer	6·0953 g./ml.
Mean density at 29·8° C.	6·0949 g./ml.
Value obtained by Richards and Boyer at 29·8° C. ...	6·0947 g./ml.
Density at 32·38° C.	6·0930 g./ml.

Values for the density of gallium at temperatures up to 1000° C. can be calculated from equation (1).

§ 7. ACKNOWLEDGMENTS

The author wishes to express his thanks to Prof. E. N. da C. Andrade, both for suggesting this problem and for his valuable help and advice throughout the work.

* The density of mercury at 0° C. has been taken as 13·5955 g./ml.

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(6) See, for instance, CALLENDAR and HOARE, *Correction Tables for use with Platinum Resistance Thermometers* (1933).

DISCUSSION

Mr J. A. HALL. I have been specially interested in the author's very neat design of the resistance thermometer, but there are one or two points which are not made quite clear in the diagram. What are the dimensions of the bulb, and in particular the width of the annular space in which the wire is wound? Are any precautions taken to prevent convection in the stem, such as the use of mica washers adopted by Callendar? It is a common fault to regard these merely as insulators, and to neglect their function as baffles. The diagram does not make it clear to me whether such baffles have been used. Has the author made any measurements of the lag constant of the thermometer? Quite apart from the special needs of the present experiments, the type of construction would seem to have advantages in minimizing lag. I do not care for the use of flexible leads with a thermometer of this type, and would prefer the use of light single-strand cable. It seems to me that the author has been a little optimistic in recording temperatures of about 800° C. to an accuracy of 0·01° C., for his constants appear to have been determined with an accuracy only sufficient to give the temperature to about 1 part in 1000. In any case, there is at present no evidence that the resistance-thermometer scale can be laid down with certainty to such a high accuracy at these temperatures.

AUTHOR'S reply. The outside diameter of the tube *C* of the resistance thermometer was 2 cm., and the width of the annular space between the tubes *A* and *C* was 2½ mm.; the length of the inner tube *A* was about 9 cm., and the length of the coil itself was 3 cm. Several pieces of mica, which can be seen in the diagram, were placed around the rod *B*, and, as Mr Hall points out, they should be regarded both as insulators for the leads and as baffles to stop convection currents. It is, however, a little doubtful whether their function as baffles is as important in this type of thermometer as it is in the usual type, because the presence of only a small annular space in the lower part of the thermometer must be of considerable help in eliminating the convection currents around the coil. I did not make any measurements of the lag constant of the thermometer. With regard to the accuracy of the temperatures given in table 1, the bridge could be read to 0·01 °C., and the temperatures have been recorded to this accuracy because the last figure in the temperature-measurement corresponds to the last figure in the height-measurement; for instance, in the case of the first dilatometer a change of 0·01° C. in the temperature is equivalent to a change of 0·0002 cm. in the height of the gallium meniscus. The absolute accuracy of the temperatures is, of course, limited by the accuracy of the calibration; the error increases with rise of temperature, and at the highest temperature (1005° C.) it is about 1 part in 1000.

537.71 538.1.081

THE DETERMINATION OF ABSOLUTE UNITS

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ABSTRACT. The International Committee on Weights and Measures, in announcing the forthcoming change of electrical units and in forecasting the values of the ratios between the new and the old units, do not say how these ratios are to be determined. There are good reasons for silence; but if the matter is to be discussed at all, it should be discussed completely.

There are two problems involved, one that of the object to which the new units are directed, the other that of the means by which that object is to be attained. The resolutions (not having the full sanction of the Committee) which accompany their statement, must be interpreted as concerning the first problem alone, if they are to be regarded as reasonable and relevant. The object of this paper is to consider the second.

For this purpose one of the many alternative methods, by which the national physical laboratories might proceed to calibrate the units, is selected and analysed with a view to determining exactly what experimental laws will be used, and how the arbitrary assumptions, necessary to fix the units, are introduced in connexion with them. The result is shown diagrammatically.

The argument leading to it is given on pp. 711–17.

Both in their identity and in their interrelations the propositions set forth in this figure are very different from those usually set forth in discussions of how absolute units are, or ought to be, determined. It is suggested that the difference is significant and is *prima facie* evidence that the usual expositions are incomplete and attain their apparent simplicity only by concealing difficulties and complexities.

§ 1. INTRODUCTION

In a recent statement* the International Committee of Weights and Measures fix the date on which "the actual substitution of the absolute system of electrical units for the international system shall take place". They says that "In collaboration with the national physical laboratories, the Committee are actively engaged in establishing the ratios between the international units and the corresponding practical absolute units"; and it gives provisional values for these ratios.

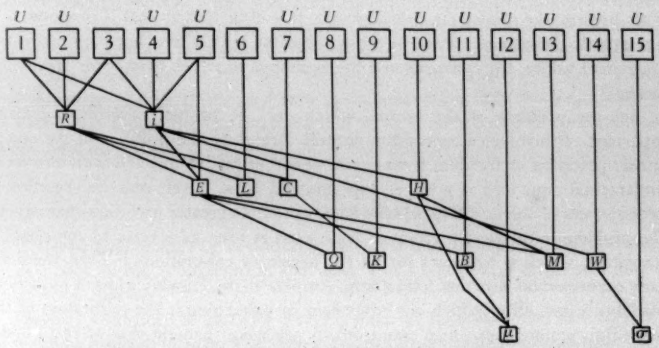
Nothing is said of how the Committee and the laboratories are going to determine the ratios. Silence on this point might well be justified on the ground that anyone conversant with the matter knows what procedure they will adopt, except possibly in respect of minor details that it is inconvenient to specify beforehand. But there is some evidence that it was due to another cause, namely disagreement within the Committee; for the statement is succeeded by certain resolutions which

* The quotations here and below are from the Appendixes to a paper by R. T. Glazebrook, *Proc. phys. Soc.* **48**, 444 (1936). They are apparently authentic; but the full documents should be read if it is desired to ascertain how far the quotations from the resolutions mentioned presently represent the views of the Committee.

(if they have any relevance to the matter) would seem to suggest a procedure by which the ratios might be determined. The Committee do not apparently take full responsibility for the resolutions; but it appears that the following sentences express opinions entertained by at least some of their members:

(*a*) "The connexion between mechanical and electrical units should be secured by assigning the value 10^{-7} in a non-rationalized m.k.s. system...to the quantity generally known as the 'permeability of space'."

(*b*) "The definitions for the principal electromagnetic units might run as follows. *Ampere.* The ampere is the constant current which, if maintained in two straight parallel conductors of infinite length at a distance of one metre apart in empty space, produces between these conductors a force equal to 2×10^{-7} m.k.s. units of force per metre length...."



1, $L=10^{-7}.\iint \frac{\cos\epsilon\, ds\, ds'}{r}$; 2, $\omega.dL/d\theta=R$; 3, R (and c) additive; 4, $F=i^2\,dL/d_3$; 5, $R.i=E$; 6, $j\rho L=R$; 7, $j/\rho C=R$; 8, $CE=Q$; 9, $C/C'=K$; 10, $i/l_1\rho=H$; 11, $E=B.\omega.dS/d\theta$; 12, $B=\mu H$; 13, $Fl=MH$; 14, $Ei=W$; 15, $W=\sigma.m.dT/dt$

It is not surprising that these propositions did not win universal acceptance. (*a*) seems to violate the elementary principle that, in order to fix the units of N quantities, N arbitrary assumptions must be made. For the Committee propose to fix at least 7 electrical units, and (*a*) make only one arbitrary assumption over those fixing the mechanical units. (*b*) proposes to jettison all the accurate methods of determining the ampere that have been worked out by generations of physicists.

The explanation is, doubtless, that the resolutions confuse the object of determining absolute units with the means by which that object is to be attained. Absolute units are such as give to the constants in "fundamental equations" convenient values, e.g. 1 or 4π or a power of ten (see further below). The problem of their object is to make the best choice of these equations and of the constants in them; the problem of the means is to find an experimental procedure whereby any given system may be assigned a value in terms of the units fixed by this choice.

Statement (*a*) apparently refers only to the object; it may be interpreted as meaning that, of the seven arbitrary choices, six are to be made on the "absolute principle", while the seventh is to be made by the alternative method of assigning a numerical value to some property of some prescribed system, namely the permeability of space. Statement (*b*) apparently refers to the means; but then (with great respect) it is nonsense. It would be sensible if it said that one of the choices was to be made so that the fundamental equation relating to the force between two current elements to their relative position has a prescribed form and prescribed constants. This equation, with six others implied similarly in the part of (*b*) which has not been quoted, would then fix the seven arbitrary choices.

If the units were to be determined entirely afresh, the problem of the object would be of great importance; but since the Committee have clearly decided not to change existing units by more than a few parts in ten thousand, it is of no importance at all, because the solution is already fixed. It is clear that all that is proposed is to give exactly convenient values to those constants which now have approximately convenient values, the constants and the equations in which they occur are already chosen.*

But the problem of the means, which may be termed *calibration*, remains important. It involves a conception entirely foreign to the problem of the object, namely precision or freedom from experimental error. Connected with any set of fundamental equations is a set of experimental laws, which may be regarded as consequences of them. Of these laws some are of far greater precision than others. The problem is to select a group of laws, each at least as precise as any possible alternative, which is sufficient for all the necessary calibrations.† Thus there are many experimental laws that follow from Ampère's law, Faraday's law of induction, and Ohm's law, all of which are equivalent in principle for the calibration of the ohm. But, among these, two stand out in precision, namely that of the Lorenz experiment and that giving the relation between a calculated inductance and a resistance. These are therefore to be preferred to others.

When these experimental laws have been selected, they—and not the fundamental equations—become the immediate basis of the units. In these days, when the foundations of our physical faith are liable to be shattered at any moment, the distinction is not wholly unimportant. It may be true that if (for example) we founded our units on the Lorenz experiment and then discovered that it was not a con-

* One reason why discussion of the object continues so fiercely appears to be that the combatants believe that theorists will actually use the important equations in the form appropriate to the official units, and that, therefore, by inducing the Committee to choose particular units, they can force everyone to adopt the form of these equations that they prefer. But their belief is utterly unfounded—fortunately so, as I believe. Theorists express their equations in such a form as to be free from constants irrelevant to their particular argument; the constants that are irrelevant depend on the argument. Thus the same writer will sometimes write Coulomb's law in a form in which the electronic charge is 1, sometimes in a form in which the velocity of light is 1. No fixing of practical units—with which he is not directly concerned—will make him abandon this convenient and excellent practice. Those who are so anxious that everyone should toe the line they draw are wasting their time in arguing with International Committees; the only thing that will achieve their purpose is severe penal legislation imposed by national governments.

† This is why objection is taken to statement (*b*). Of the consequences of the fundamental equation, that selected is known to be far inferior in precision to others.

sequence of the fundamental equations, the whole problem of units would be reconsidered, and that therefore it is unnecessary to consider this possibility. Nevertheless, there seems to me some interest in inquiring what are the experimental laws that are likely to form the true basis of the units that the Committee propose to adopt. That inquiry is the main purpose of this paper.

Strictly it should include a consideration of all the good alternative methods for the absolute determination of the ohm, ampere, etc. But my concern is with principles rather than with details; I want to inquire whether the experimental laws that will be the immediate basis of the units can be arranged in some sort of logical scheme, such as is often proposed for the fundamental equations which may be held to form their ultimate basis. Accordingly only one way of calibrating the units will be discussed; it will suffice if it is a reasonable method and likely to form part at least of the actual method, which will doubtless embrace many alternatives. Further, some instructions concerning the object of the units must be assumed. It will be assumed that they are contained in statement (*a*), as interpreted above, and that "non-rationalized" implies that the "convenient value" is always to be 1. Lastly, some quantities will be introduced into the scheme other than those discussed by the Committee, and it will be assumed that all of these are also to be determined by the absolute method.

§ 2. THE EXPERIMENTAL LAWS

It will be well to start by considering generally how an experimental law determines a unit by the assignment of the value 1 to a constant. The process may be described as follows.

We find a number of systems S and a piece of apparatus into which each of them can be inserted in turn. The systems must be identifiable and distinguishable. The distinction may be made by the varying values of a measurable property possessed by each of them, so long as the measurement of this property does not involve the law under consideration; on the other hand it may be made by properties which are not measurable. S

The apparatus must be characterized by two measurable properties x, y, and by an identifiable state P (which is usually some form of equilibrium) assumed, for a given value of x, when and only when y has some particular value. P

We insert each system S in turn in the apparatus, and determine the pairs of values (x, y) for which the apparatus assumes the state P. We find on examination that these pairs of values are related by the algebraical equations

$$f(x, y) = C \qquad \text{.....(1)},$$ f, C

where C differs according to the member S inserted and C_r is characteristic of the member S_r. C is then a measurable property of the systems S. C_r S_r

The value of C_r depends upon the units used in measuring x, y. We may express this fact by rewriting (1) thus

$$f(x, y) = C' . X \qquad \text{.....(2)},$$ C'

and adopting the convention that, when the units of x, y are changed, only C' is to be changed. X_r is then a characteristic of the system S_r only. There is still an ambiguity; for C_r can be divided into C' and X_r in many ways. This ambiguity can be resolved by two methods. One is to choose arbitrarily some system S, say S_1, and assign to it some value X_1 (say 1); then C' is determined by facts. Alternatively we may choose arbitrarily one pair of units of x, y, and assert that C' has some value, say 1, for these units; then *every* X_r is determined by facts. Absolute systems of units are those in which the second procedure is adopted widely (though not always universally).

It is to be observed that the symbol $=$ in equation (1) expresses far more than a numerical relation; it implies also the nature of the apparatus and the state P. Again, in an absolute method, the system S_1, to which the value 1 is attributed, is not distinguished in any way from other systems S. Neither of the terms "equation" and "unit" indicates accurately the essentials of the procedure.

No complete system of measurement can be established by this process alone; for the process implies that some properties, namely x, y, are already measurable. Somewhere in the background must lie another process, depending on laws that are not numerical. These are always laws of addition, which state that certain combinations of two system S are equivalent, in a special sense, to a third member; such laws are the basis of all measurement, but do not themselves involve measurement. Laws of this kind are often used in conjunction with numerical laws, of the type (1), in a manner that will appear from the example we are going to discuss; it is fatal to overlook them.

We can now start on our task of attempting to order in the light of these principles a procedure that the standardizing laboratories might adopt in establishing their calibrations. Of course it is impossible, in a reasonable space, to set forth the matter completely; only the salient features will be discussed.

The instructions assume that we can measure mass, length, and time, and assert (as three of the arbitrary assumptions) that the units are to be the kilogram, metre, and second. We shall have to assume further (though much might be said on the matter) that it follows necessarily that we can measure force, power, angle and area; the units of force and area must be 10^5 dynes and the square metre. We introduce
L at once the fourth assumption prescribed explicitly by defining a quantity L appertaining to a pair of linear conductors of, and surrounded by, non-magnetic material. At present this is a pure definition; but it becomes a physical assumption as soon as we use the definition. The definition of L is

ϵ, s, r
$$L = 10^{-7} \cdot \iint \frac{\cos \epsilon \; ds \; ds'}{r} \qquad \ldots\ldots(3).$$

The meaning of the symbols is too well known to be stated; it has only to be observed that L can be determined by measuring lengths and angles alone. We can also
θ measure $dL/d\theta$ and dL/dz, where θ represents rotation of one conductor in relation
z to the other while z represents relative translation, for a determinate value of θ or z.

But a question naturally arises. How are we to know whether materials are conducting or non-magnetic? It has to be admitted that there is no evidence that we could ever have arrived at our present methods of determining these matters without a knowledge of laws to be introduced later. But such knowledge is not essential in principle. For the determination requires no measurement; we have merely to introduce the material into suitable apparatus (different according as we are inquiring into conductivity or permeability), and notice whether there is any change; we have not to measure the change. Again, in order to decide what apparatus is suitable, we cannot require a knowledge of the absolute units we are seeking; for our present ideas on the subject were fully developed before any question of absolute units arose. Accordingly, though it would be very difficult to explain the method without circular arguments, it is almost certain that the task is feasible. Similar questions arise at almost every stage; they will not be mentioned again.

Resistance. We now start our first experiment (Lorenz apparatus). The systems S (resistors) are bodies identified as individuals. Of a pair of linear conductors to which L appertains, we connect one, A, in series with a source of current (which need not be measured) and with each S in turn; and we connect the other, B, in a circuit, containing a galvanometer. Joining the ends of S*, P means that no current passes through the galvanometer. That defines the apparatus. If we measure ω, the relative angular velocity of A and B, we establish the law

ω

$$\omega \, . \, dL/d\theta = C \qquad \ldots\ldots(4).$$

The assumption made is that we are to write $C = 1 \, . \, R$; R (ohms) is then a measurable property of the resistors.

R

This method of measuring R is precise only when R lies within a certain range. To measure R for all resistors, we must establish the additive properties of R. We discover that we can find triplets, S_1, S_2, S_3, such that if S_1 and S_2 are connected in series, they are equivalent to S_3 in the sense that the substitution of one for the other produces no change in a suitable apparatus. We find further that, in virtue of this fact we can assign numerals s to the resistors consistently, so that in such a triplet $s_1 + s_2 = s_3$. If we assign the numeral 1 arbitrarily to one resistor, we can then measure a property R' of the resistors, quite independently of equation (4) or any other numerical law.

R'

We now find that, in the range within which equation (4) is applicable, R' is proportional to R; if we use for R' the unit that we have established for R, R' and R are identical. In a similar way we discover the additivity of conductivity c, and make c equal to $1/R$. In future we use equation (4) only to establish the unit; all measurement in terms of this unit is done by the process depending on the additivity of resistance and conductivity.

c

Current. In our second experiment the systems S are silver voltameters in which silver is deposited at different rates; since we can measure mass and time, these can be identified. The apparatus is a balance by which forces can be applied

* The use of the radius of a disc for B is a more practical device, which requires no special consideration.

z along z between the two linear conductors to which z refers; P is equilibrium; a
F voltameter S is in series with both conductors. If we measure the force F and dL/dz, we can establish the law

$$F = C.dL/dz \qquad \text{.....(5).}$$

i The assumption made is that we are to write $C = 1.i^2$; i (amperes) is then a measurable property of the voltameters. We may proceed, if we wish, to prove that i so measured is proportional to the rate of deposition of silver within a certain range; but this law is not essential to the procedure.

The fact that the proportionality is not universally valid (e.g. for very large currents) suggests that again we should use equation (5) only to establish the unit, and use some other law for measuring i. But it is not now convenient to use a method based on addition. Actually i is additive in branched circuits; but measurement based on that property is inconvenient and not precise. We must leave this problem for the moment. But it is to be observed that we can justify our decision
i' to write $C = i^2$, rather than $C = i'$, on the ground that i, defined by the first convention, and not i', defined by the second convention, is additive, and is therefore the more important quantity. However, this example makes it clear that the application of the convention of absolute measurement requires more than the decision to make constants unity; it requires also the choice of the function of the measurable quantity which that constant shall multiply. Accordingly if an absolute system is to be expounded completely, the convention implied should be stated explicitly *in every case*.

Potential-difference. The systems here are voltaic cells. The apparatus need not be described. Measuring R and i by the methods already established, we find

$$R.i = C \qquad \text{.....(6);}$$

in accordance with the absolute convention we take C (volts) as being the measur-
E able property E of the cells. E turns out to be additive for cells connected in series; this proposition is used in accurate measurement, but it is not required to extend the range of E. For since a resistor having any value of R can be obtained, all E's can be measured by means of a current within the voltameter range. However we can use equation (6) to extend the range of current-measurement, and yet base our extension of the meaning of current on facts and not on a mere definition. For if we write equation (6) thus

$$E/R = C \qquad \text{.....(6'),}$$

we can prove that this law is valid outside as well as inside the voltameter range, if currents outside can be identified, and thus measure currents by a method valid over a much wider range. This is the actual process of measurement; equation (5) merely defines the unit.

It would be tedious to proceed throughout with the same deliberation. The remaining quantities will be discussed more summarily, and many questions, similar to those already raised, will be ignored.

Inductance. The unit is defined by equation (3) applied to certain simple forms. Measurement in terms of this unit depends upon the law

$$jpL = R \qquad \text{.....(7),}$$

which can be proved, and needs no arbitrary assumption.

Capacity. Here, on the other hand, the law*

$$j/pC_0 = R \qquad \text{.....(8),} \qquad C_0$$

both defines the unit, by the assignment of the value 1 to the constant, and provides the method of measurement.

Quantity of electricity is both defined and measured by suppressing the constant in the law.

$$C_0 V = Q \qquad \text{.....(9).}$$

Dielectric constant. We define a geometrical quantity C_0' ("electrostatic capacity *in vacuo*") for some simple condenser; among geometrically similar systems it is proportional to length. We establish the law that C_0' is proportional to C_0, as just defined; the constant ratio C_0/C_0' is defined as the dielectric constant. Of course it does not turn out to be 1 for a vacuum. C_0'

Magnetic quantities. These present some difficulty. The International Committee propose to fix only one magnetic unit, namely the weber, the unit of flux ϕ. Concerning the remainder there appear to be unresolved differences concerning the object of the units. Thus those directly interested do not seem to be agreed by what fundamental equations the gauss and the oersted ought to be related to the other units and to each other, or (what comes to the same thing) what quantity if any these names should denote. I shall therefore merely assume that quantities usually denoted by B and H are to be defined somehow by the absolute method, that is, by assigning a convenient value to constants in an experimental law; but I shall give them no name and shall leave undetermined the convenient value Z in the experimental laws I shall choose. Incidentally this procedure has the advantage of making it clear that the absolute method is not really confined to the choice of 1 (or even of 1 and 4π) as the convenient value. ϕ Z

A further difficulty is that magnetic quantities are vectors. A mass of verbiage would be necessary to state the matter accurately; the assumption that all quantities are similarly directed will simplify the statements greatly and will mislead nobody; accordingly I shall make it.

The only systems for which calibrations in respect of H and B will be required are systems of magnets producing fields uniform over a considerable volume. We start by defining a geometrical quantity $1/l_h$, characteristic of a linear conductor, which in similar systems is inversely proportional to length. Various formulae for it are given, all equivalent in the relevant cases. One of them is l_h

$$1/l_h = \int \boldsymbol{ds}' \times \boldsymbol{r}/r^3 \qquad \text{.....(10).}$$

We establish the law that, if the arrangement of magnets and the linear conductor are placed in suitable relative positions, and if l_h and the current i through the linear

* C_0 is written with a suffix for capacity, in order to distinguish it from C in equation (1).

conductor are varied, then, in the state P such that no couple is exerted on a suitably placed magnet,

$$i/l_h = C \qquad \text{.....(11).}$$

H We write $C = Z.H$.

We next take a coiled linear conductor, whose turns embrace effectively the area S. We place this conductor in the field of the arrangement of magnets, rotate it at angular velocity ω and measure the potential difference E between its ends when the normal to the effective area is in some fixed direction relative to the arrangement. We establish the law

$$E = C.\omega.dS/d\theta \qquad \text{.....(12).}$$

We write $C = Z.B$.

If, in a given arrangement of electromagnets, we vary i, the magnetizing current, and measure B and H, we find that, within a certain range,

$$B = C.H \qquad \text{.....(13),}$$

μ We write $C = Z.\mu$.

If we place a magnet in a variable field H, we establish the law, valid within a finite range,

$$F.l = C.H \qquad \text{.....(14),}$$

where $F.l$ is the couple on the magnet. We write $C = Z.M$. M is then the magnetic moment.

There remains the weber, the one magnetic unit that the Committee do propose to fix. I can find no experimental law of any reasonable precision in which flux ϕ is a constant. Thus the resolutions mentioned above propose that the weber is to be "the magnetic flux which, when linked with a circuit of a single complete turn, would produce in that circuit an electromotive force of one volt if reduced to zero in one second at a uniform rate". But, if we have not measured flux, how are we to determine whether its rate of reduction is uniform? And, even if this difficulty could be overcome, a flux which is being reduced at a uniform rate is clearly not a constant of an experimental law describing that experiment. Perhaps there is a way of avoiding this difficulty; but meanwhile it appears that flux ϕ must be regarded as a mere name for the quantity $\int BdS$, the selection of that name not being dictated by any simple and unitary experimental law. If this is so, the assignment of a value to the weber is only a roundabout way of assigning a value to C in equation (12), which defines the unit of B. Accordingly no more need be said about it.

The watt. We establish the law that if the passing of a current i through a potential-difference E generates the same amount of heat (i.e. produces the same thermal change) as the dissipation of W watts of mechanical power, then

W

$$E.i = W \qquad \text{.....(15).}$$

This is a universal law, valid for all systems to which it applies at all; there is no constant C variable with the system, and therefore no call for any arbitrary assumption concerning its value. However, there is something arbitrary in giving a special name to the product Ei, rather than to any multiple of it; accordingly the definition of the watt as Ei may be taken (though with some hesitation) as one of the arbitrary assumptions of our system.

However, the important matter in practice is the relation of the watt to some quantity used in calorimetry, say the specific heat of water; this is what requires calibration. We establish the law

$$W = C.m.dT/dt \qquad \text{.....(16)},$$

where m is the mass and T the temperature of water in the neighbourhood of (say) 15° C. The specific heat of water is the quantity obtained by writing $C = 1.\sigma$ in this equation. (The measurement of temperature has to be assumed, but this is not an electrical quantity.) σ, T

§ 3. DISCUSSION

The survey that has been made is summarized in the diagram. Here the large numbered squares are the quantitative propositions that have been used; they are identified by their numerals on the right. Purely qualitative propositions, such as were discussed on p. 713, are ignored. Those propositions in which an arbitrary assumption is made for the purpose of fixing units are distinguished by a *U*. The quantities discussed are denoted by the small squares; lines connect them to the propositions on which their measurement depends. They are arranged in generations represented by the horizontal rows, such that a quantity in one generation depends on at least one quantity in the previous generation. It will be observed that the only two propositions on which all the quantities depend are the definition of mutual inductance and the additivity of resistance (and conductivity); neither of these is a numerical law, and neither of them therefore involves the assumption of absolute measurement in its typical form.

There is evidently a profound difference, not only in identity, but also in interrelation between the laws that form the immediate basis of any experimentally determined units and the fundamental equations (which I should term "theory") that are so often offered as their ultimate basis. We have found no evidence that "it is possible to deduce all electrical quantities from (one single quantity) by means of a series of equations in each of which one and only one new electrical quantity appears".* The relations that we have found are much more complex, and would be more (and not less) complex if we had taken account of all the alternative procedures that will doubtless play some part in determining the Committee's final choice of the ratios.

From this difference many persons will probably draw the conclusion that we should fix our eyes steadily on these beautifully simple relations and ignore all the untidy and unpleasant work that the staffs of the national physical laboratories will have to perform for our benefit. But my conclusion, though the need for brevity forbids me to support it fully, is very different. It is that all this beautiful simplicity is delusive and attained only by ignoring essential matters. If we were so indelicate as to inquire precisely what these equations mean and what is their relation to experiment (surely they must have *some* relation), the stately fabric would dis-

* These are the words of a correspondent quoted by R. T. Glazebrook, *Proc. phys. Soc.* **48** (1936), 452.

integrate; it would be found that that simple "=" covers a multitude of complexities, and that many propositions are implied that are not expressible by so-called equations at all. The illogicalities discussed on p. 713 would reappear, not in the crude nudity of the "classical" exposition,* but still merely half-hidden behind decent coverings. There may be no logic of science—I do not think there is—but there is yet a distinction between sound and thorough exposition of the foundations of measurement and summaries that are specious merely because they are full of circular and fallacious arguments.

DISCUSSION

Dr E. H. RAYNER. We are all glad to see Dr Campbell and to have a paper by him on such a subject as the philosophy of units.

In the first place I do not think that Dr Campbell's definition of absolute units on the second page of the paper agrees with the recognized meaning of the term. He says that "absolute units are such as give to the constants in 'fundamental equations' convenient values, e.g. 1 or 4π or a power of ten". Actually the meaning of the term "absolute" was defined by the B.A. Committee in 1863 as follows:

> "The word 'absolute' in the present sense is used as opposed to the word 'relative' and by no means implies that the measurement is accurately made or that the unit employed is of perfect construction; in other words it does not mean that the measurements or units are absolutely correct but only that the measurement, instead of being a simple comparison with an arbitrary quantity of the same kind as that measured, is made by reference to certain fundamental units of another kind treated as postulates."

This paragraph is reproduced by the late Sir R. T. Glazebrook in a note on the three absolute systems of electrical measurements.†

Dr Campbell is under a serious misapprehension when he imagines that the work of scientists over many years is to be scrapped. The reverse is the case. The present so-called international units are only of a stop-gap character. They are quite empirical, being defined in terms of the rate of deposit of a mass of silver in an electrolytic cell and of a nominal value which is ascribed to the specific resistance of mercury. They were adopted to achieve a high measure of agreement between the units of different nations. The units so obtained are intended to be very nearly the same as the corresponding absolute units, which are the ideal but have not until recently been realized with adequate accuracy on account of the technical difficulties involved. The absolute units which are to come into force in 1940 will be in no way dependent on the present units, as Dr Campbell imagines. The approximate values of the ratios which he mentioned have been published in order to prepare the public and the instrument-makers for the change.

* The classical exposition starts from charges and poles. How a charge is to be distinguished from a pole is never explained, except possibly by the statement that poles do not exist.

† *Proc. phys. Soc.* **48**, 450 (1936).

As an example of the alteration involved, a resistance of 100,000 ohms according to the present size of unit will be approximately 100,050 ohms in absolute units. Every resistance will have to be shortened to acquire the same numerical value in the new unit. The significant figure after the 5 may be more definitely given at a later date.

As Dr Campbell says, writers in many countries have discussed the electrical units and their basis during the last few years. As regards the mode of realization, few of those who have been writing on the subject have seen instruments for generating the units, and still fewer have handled them. While philosophical discussion of the subject is all to the good, it must not interfere with or dictate the method of realization. The recent literature on the subject has not in any way modified the methods of realizing the units, as carried out in the few national laboratories cooperating in this work.

No standard method is prescribed, such as is necessary to obtain a high degree of agreement in realizing the present empirical units. In fact the apparatus for generating the ampere and the two methods for generating the ohm at the National Physical Laboratory are unique. No other Laboratory uses the Lorenz machine or the Campbell mutual-inductance method for the ohm, and no one else uses a Kelvin type of balance. Other nations are using the Rayleigh pattern. All the balance methods require a knowledge of the local value of gravity.

In practice the basic quantity is inductance, which has the dimension of length only, and the value is arrived at from linear measurements of the apparatus, which have to be determinable with high precision. To arrive at the unit of resistance the dimension of time has to be added. This is done as a speed of rotation of part of the apparatus in the Lorenz machine and as an alternating-current frequency in the Campbell method. It happens that resistance is one of the most important scientific and engineering electrical quantities, and portable realizations of it over a very wide range of values can be constructed with high precision. The fundamental unit as realized is at once the basis of the most important technical quantity.

For the evaluation of current in absolute measure, the quantity *force* has to be dealt with, and it requires the addition of the dimension mass. The great sensitivity available in a balance has led to its use for the measurement of the electromagnetic forces. The force available is small, only of the order of 1 part in 1000 of the dead weight carried by the balance; but the perfection of the apparatus enables it to be measured to the order of 1 part in a million. In practice, however, a portable ammeter, accurate to the order of 1 in 100,000 or in 10,000, is not available, so that the ampere is not a practicable engineering reference unit. Simple electrolytic cells of great stability and reproducibility of voltage happen to be available. Their voltage is determinable in terms of the absolute ampere and ohm, whence they are universally employed as practical standards of voltage; and they form the second engineering type of portable unit.

Dr L. Hartshorn. As one who is closely concerned with attempts to determine electrical units with precision, I have long felt that the experimental foundation for

the fundamental laws of our text-books was by no means obvious. Dr Campbell's exposition is the only one I have ever met which could claim to be based on facts of the kind which can be verified with the precision expected of a modern electrical laboratory. I am reminded of an attempt I made some three or four years ago to write out definitions of the ampere, ohm and volt in terms which could be upheld in either an electrical laboratory or a court of law. After reading Dr Campbell's paper I was sufficiently curious to look up these attempts at definitions and I think that of the ampere is sufficiently in line with Dr Campbell's argument to be worth quoting.

> "*The ampere* is the tenth part of that unvarying electric current which, when traversing each of two linear circuits having a common axis of symmetry and located in free space, causes them to act upon one another with a force the value of which expressed in dynes is numerically equal to the rate of change of mutual inductance of the two circuits with respect to a displacement of one relative to the other along the common axis of symmetry. *The mutual inductance* of two linear circuits in free space is given by the following integral extending round both circuits
>
> $$\iint \frac{ds\,.\,ds'\cos\epsilon}{r},$$
>
> where ds refers to an element of one circuit, ds' an element of the other, ϵ is the angle between the two elements and r is the distance between them."

Although this definition satisfied me at first, as not involving unit poles or abstractions remote from actual experience, I was subsequently disturbed by the reflection that the linear current which is implied, and which Dr Campbell also uses, is an abstraction which can never be realized. If we use very thin wires in order to approximate more closely to the conception we introduce another difficulty: the resistance of the wire increases and therefore the electric field associated with any current through the wire becomes sufficiently important to disturb any measurements of the kind in which the magnetic effects only are wanted. I should be interested to know how Dr Campbell would deal with these difficulties. Possibly they would appear as a limitation to the accuracy of verification of equations (7) and (8), but I can well believe that even with such a limitation these laws have been verified with a higher accuracy than could be claimed for possible alternatives.

I well remember the late Sir Joseph Petavel's comment on my proposed definitions. It so well summed up my own feelings on the question. He merely said in the pleasantest possible manner "I hope it won't be necessary to use them." If I were a member of the International Committee on Weights and Measures, I think I should feel exactly the same about Dr Campbell's scheme, although from a purely scientific point of view I am entirely in agreement with it. What such a committee should say is partly an administrative question, and it is at least arguable that since the pronouncements of the committee are mainly intended to coordinate the measurements of workers in various countries, they will be most effective if expressed in terms of the current working ideas, and, in the case under discussion,

the simple generalizations of our text-books, with all their concealed difficulties and complexities. However, the Physical Society is far more concerned with the foundations of scientific knowledge than with the problems of standardization, and there can be no question that this paper goes a long way towards clearing away the debris from the foundations of electrical measurements.

I observe that Dr Campbell discourages the idea of a definitive system of units for all purposes. I agree that theorists should continue to express their equations in such a form as to be free from constants irrelevant to their particular argument, and this means that they should be free to vary their units as may be convenient. However, I feel that it would be a great convenience to scientific workers if all numerical data were expressed in terms of one preferred system, and if the equations corresponding to this system were employed universally for theoretical work of a technical character, which must ultimately deal with numerical values of the quantities of ordinary laboratory experience. I do not see any advantage in the use of the electrostatic and electromagnetic C.G.S. systems along with the practical system for such work, and I think that experimental physicists and electrotechnicians would find it convenient to have one preferred system on the lines proposed by Giorgi and G. A. Campbell. It is regrettable that the recent flood of literature on the subject is such as might discredit the proposal.

Mr J. GUILD. I must strongly support Dr Campbell's contention that it is the experimental laws underlying practical methods of measurement which give significance to the results of measurement and not the "beautifully simple relations" and abstract concepts on which the significance is usually assumed to depend. This would also appear to be the view of the late Sir Richard Glazebrook, as I interpret his paper on the fourth unit of the Giorgi system of electrical units,* admirably summarized in his last sentence: "We must distinguish between methods of measurement...and the mathematical theory of electricity." I believe that a clearer understanding of the meaning of measurement—and therefore of the significance of the quantitative data on which all theory of the behaviour of things has to be based—would be brought about if the official definitions of important scales of magnitude were shorn of all reference to ideal systems which, in the nature of things, cannot exist, and which have no relevance to the sordidly practical problems of measurement. I think we have gone too far, in the past, in the attempt to rid our metrical systems of what Dr Rayner describes as "the trammels of empiricism". It seems to me that to attempt to rid measurement of empiricism is to attempt to rid it of its essential characteristic. Measurement is necessarily empirical if it is to fulfil its purpose of providing quantitative data which shall be independent of any theory into which those data may subsequently be fitted. Its empirical nature should be advertised and not concealed by a veil of abstractions which, far from lending dignity to measurement, imposes on it the indignity of sailing under false colours.

The practical object of arriving at a choice of units which will avoid the occurrence of arithmetically awkward factors in physical relations involving the more

† *Proc. phys. Soc.* **48**, 452 (1936).

important magnitudes is, as Dr Campbell points out, a mere matter of convenience, having nothing to do with the rightness or wrongness of the units selected. The aim has gradually been achieved, to an ever increasing order of accuracy, by the process of trial and error in the standardizing laboratories, and cannot be achieved any other way, definitions notwithstanding.

AUTHOR's reply. Dr Rayner is right in saying that, in 1863, the object for which absolute units were proposed (and from which they derived their name) was the avoidance of any need for material intercomparisons; the assignment of values to arbitrary constants was a mere means of attaining the object. But the object has proved unattainable, because intercomparisons are more precise than absolute determinations; the assignment of the constants has therefore become the primary object. The statement of the International Commission is, in effect, an instruction to the standardizing laboratories to choose their material standards, by comparison with which all measurement will actually be made, so that the constants approach the assigned values within the least possible experimental error.

I cannot discover in my paper any signs of the delusions of which Dr Rayner suspects me. One of my main purposes is to point out that eminent persons do not always mean what they say.

Dr Hartshorn's point about linearity is interesting. The ideal conditions contemplated by simple theories can never be realized, but departures from them may be concealed by experimental error. Whether they are concealed in any particular case is a question of fact. Thus if, when we calculate L on the assumption that the conductors are linear, we find systematic errors, not concealed by experimental errors, in laws (4) and (5), then, and only then, we must make "corrections" for non-linearity by using a more complicated theory. The simple scheme proposed then breaks down; but the main conclusion, that the relation between units and fundamental equations is very complicated, is confirmed. It is interesting to note that one of the propositions that would have to be added is that currents are additive.

Unless it is seriously proposed to change the units by large factors, in order to produce a set that everyone can be persuaded to use, the questions how far uniformity is desirable and how it may be attained are irrelevant to this discussion. The best way to secure that all numerical results shall be stated in the official units would be the publication of a very complete conversion table, which would take into account all the forms of the fundamental equations that anyone is likely to use. Conversion tables published hitherto have always been incomplete, because the author's main aim has been to argue that some particular form is better than others; moreover, the tables have been confused by obscure irrelevancies about dimensions.

I agree entirely with Mr Guild.

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THE STRUCTURE OF SOME METALLIC DEPOSITS ON A COPPER SINGLE CRYSTAL AS DETERMINED BY ELECTRON-DIFFRACTION

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ABSTRACT. Nickel, copper, zinc, cadmium, silver, chromium and cobalt were deposited electrolytically on etched copper single crystals and the structure of the deposits was found by electron-diffraction. At small current densities the layers are oriented except in the case of zinc and cadmium. The nickel and cobalt deposits give patterns containing additional spots, lines and irrational spots. It is shown that these are accounted for by assuming the occurrence of repeated twinning on (111) planes, the additional spots being due to twinned lattices and the lines due to twin planes. The twin planes must be considered separately and not simply as part of the lattices on either side of them. The thin sheets of lattice thus formed give rise to the irrational spots observed. Finally, a discussion is given of the factors determining the orientation of a layer of metal on the copper crystal.

§ 1. INTRODUCTION

The oriented overgrowth of one crystal on another is well known in the case of ionic crystals. Similar phenomena occur with metallic crystals and may often be investigated very conveniently by means of X rays[1] or electron-diffraction. Using the latter, G. P. Thomson[2] showed that a copper compound is oriented in a definite way on the etched face of a copper single crystal. Later, Farnsworth[3] deposited silver on a gold crystal and found that the silver film had the orientation of the gold crystal. Cases have also been reported by Finch and Quarrell[4] where a deposited metal suffers a change from its usual lattice dimensions in order to conform, across the contacting planes, with the underlying material.

The continuance of the structure of the underlying metal by the deposit has also been studied in other ways. Blum and Rawdon[5] showed clearly, by the microscopic examination of etched sections, that the crystal grains at the surface of a piece of cast copper were continued by a deposit of electrolytic copper. Later workers have shown that this phenomenon also occurs when the deposit and the base are of different metals[6].

The present paper describes the results obtained when various metals were deposited on the etched face of a single crystal of copper. G. P. Thomson's method of attack was again employed and the deposition was accomplished by electrolysis of the usual electroplating solutions.

Before proceeding to describe the experiments, reference will also be made to the results of Kirchner and Lassen[7]. They evaporated silver on to a rock-salt cleavage face and examined the surface by electron-diffraction. The results showed that the silver was oriented as a single crystal with its cube face parallel to the rock-salt cleavage plane. The pattern from the silver consisted generally of the usual cross grating of spots. For some thicknesses of silver, however, certain of the spots observed were not in the positions to be expected but occurred, for example, in groups of four, symmetrically placed around the normal positions. These spots were named *irrational spots* and an explanation of their appearance was given by Kirchner and Lassen, who showed that they could be considered as arising from octahedral planes acting as cross gratings inclined to the electron beam. It was also suggested that the octahedral planes, being most densely packed with atoms, would tend to act in this way. This matter is referred to later in the sections dealing with nickel and cobalt.

§ 2. GENERAL EXPERIMENTAL PROCEDURE

The electron-diffraction apparatus was of the well-known Thomson-Fraser[8] type with a camera-length of 28 cm. The crystal specimens were cut from a rod 6 mm. in diameter. The surfaces of the specimens were ground on 0000 emery paper and etched for 5 min. in a 10-per-cent solution of ammonium persulphate. They were washed for a few seconds under tap water, then placed in alcohol and finally in benzene. Before the plating of the specimens, diffraction photographs* were taken from the copper surface alone to ensure that this was perfectly clean. These photographs showed the usual cross grating of sharp spots. The first specimen cut also showed Kikuchi lines, but these did not occur in later specimens. G. P. Thomson[2] has shown that the cross-grating pattern is due to small projections on the crystal surface, these projections or lumps being crystallographically coherent with the main crystal. He has also discussed the fact that etched metal crystals do not as a rule show Kikuchi lines and he attributed this to distortion of the lattice[9]. Since a copper single crystal is rather soft, it was found difficult, in the present experiments, to avoid slight bending of the rod during sawing. This did not appear to result in any change in the spot patterns, but evidently, according to Thomson's theory, the distortion produced must have been sufficient to cause the disappearance of Kikuchi lines.

The plating circuit was of simple type and the anode of the plating cell was a cylinder of the same material as the metal being deposited except in the case of chromium, in which a lead anode was used. The composition of the various plating solutions is stated later at the end of this section. These solutions do not present any features worthy of special mention. There was no agitation of the solutions during plating and the operations were carried out at room-temperature. In many cases it was evident that Faraday's laws of electrolysis did not apply and the thick-

* These, and later photographs, were taken with the beam at almost grazing incidence on the surface of the specimen.

ness of the deposited layer could not be determined in this manner. In most cases the thickness stated must be regarded as only approximate.

Details of the various plating solutions and anodes are given in the table.

Table

Metal	Plating solution in g./litre	Anode
Ni	300 $NiSO_4.6H_2O$ 3·1 NaCl 6·2 H_3BO_3	Ni
Cu	200 $CuSO_4.5H_2O$ 30 H_2SO_4	Cu
Zn	96 $ZnSO_4.7H_2O$ 4 NaCl 6 H_3BO_3	Zn
Cd	400 $3CdSO_4.8H_2O$ 3·5 NaCl 7 H_3BO_3	Cd
Ag	0·26 $KAg(CN)_2$ 0·02 KCn	Ag
Cr	400 CrO_3 2 H_2SO_4	Pb
Co	300 $CoSO_4.7H_2O$ 3 NaCl 6 H_3BO_3	Co

§ 3. NICKEL ON COPPER CRYSTAL

Experiments performed. In all cases the etched (110) face of the copper single crystal was used as base. (i) A film of nickel of 20 A. thickness was deposited at a current-density of 0·3 mA./cm.^{2} The electron-diffraction pattern showed spots as in the original copper pattern and also faint rings due, apparently, to polycrystalline nickel. Similar effects were observed for thicker films of nickel deposited at the same current-density. When 200 A. had been deposited, the rings and spots were approximately equal in intensity. (ii) The current-density was increased to 3·25 mA./cm.^{2} and the results were similar to those obtained at 0·3 mA./cm.^{2} (iii) The current-density was increased to 10·5 mA./cm.^{2} and the deposit was of the same nature as in the first two cases. (iv) The current-density was lowered to 0·025 mA./cm.^{2} No rings were observed in the resulting diffraction patterns. When 60 A. had been deposited, the pattern was the same as that obtained from the original copper, but when the thickness of nickel was increased, new characteristics appeared. These were best studied in the two important azimuths of the (110) face (*a*) when the electron beam was approximately parallel to the diagonal of the cube-face, and (*b*) when the electron beam was approximately parallel to the edge of the cube. When 230 A. had been deposited, there was no change from the normal pattern in azimuth (*b*) except a slight loss of sharpness in the spots. In azimuth (*a*), however, there were lines running through the spots, forming a diamond-shaped

pattern, and additional spots lying on these lines, figure 6. The lines became more and more prominent as the thickness of the nickel was increased still further to several thousand angstroms and this was accompanied by a small amount of elongation in some of the additional spots, in the direction of the lines on which they were situated. When 1000 A. had been deposited, the pattern in azimuth (*b*) was completely changed from its normal form. Each spot was replaced by two irrational spots placed vertically one above and one below the normal position, figure 7. (v) At a current-density of deposition of 0·015 mA./cm.^{2}, the results were the same as at 0·025 mA./cm.^{2}

Explanation of results. It appears from (i), (ii) and (iii) that, when nickel is deposited on the etched face of a copper single crystal at current-densities of 0·3 mA./cm.^{2} or more, the layer of nickel is polycrystalline with the usual face-centred cubic structure. The rings appear to pass through the copper spots in the case of thin layers, so that it must be presumed that the first layers of nickel have the same lattice constant as copper. Measurements (based on the formulae $d=L\lambda/r$ and $\lambda=h/mv$) on a plate taken from a layer of nickel 500 A. thick gave a value for the lattice constant of 3·58 A., which seems slightly high compared with the X-ray value of 3·517 A. Doubtless the nickel gradually reaches its normal structure as the thickness is increased.

The results obtained at low current-densities, (iv) and (v), show that, for small thicknesses of the order of 60 A., the nickel is oriented in exactly the same manner as the underlying copper single crystal. In the case of greater thicknesses, of 1000 A. or more, it will be convenient to consider the two principal azimuths separately. The pattern obtained with the beam parallel to the cube-face diagonal is best regarded as made up of five parts. These are indicated by circles, triangles, squares, full lines and dotted lines in figure 1. Certain of the spots, indicated by black circles, for example those lying on the line *ab*, are common to two or more patterns. Underneath the pattern in figure 1 is shown the (110) face of the specimen. This, as already explained, is not perfectly plane but covered with small lumps. In this particular azimuth a possible and indeed probable section of a lump on the (110) face is a small triangle bounded by (111) and (11$\bar{1}$) planes as shown in figure 1. The electron beam is considered to be moving in a direction normal to the plane of the paper. The other bounding faces of this lump may be left undefined. The pattern of spots indicated by circles is clearly due to nickel forming on the various lumps in conformity with the copper (main pattern). The pattern indicated by squares may best be regarded as arising from layers on the octahedral face *AB*. This pattern may be derived from the main pattern by revolving the main pattern through 180° about the line *ab*. In this case, the spot *d* of the main pattern becomes the spot *e* of the pattern of squares. Alternatively, the spots of the main pattern may be reflected across the line *ac*, produced if necessary. It is at once seen that spot *f* of the main pattern then becomes spot *g* of the pattern of squares. The line *ac* is perpendicular to *ab* and parallel to the octahedral plane *AB*. The pattern indicated by small squares is therefore formed from a nickel lattice twinned on (111) planes of previously deposited nickel (Spinel twin). In the same way it can be shown that

the pattern indicated by small triangles, figure 1, arises from nickel twinned on (11$\bar{1}$) planes, such as *CD*. To obtain the line pattern indicated by full lines, figure 1, we require a plane of atoms lying parallel to the electron beam and normal to the direction of the lines. Since the lines lie perpendicular to the face *AB* this suggests that the twin plane is acting alone to produce the line pattern. The fact that the twin pattern and the line pattern increase in intensity together as the thickness of the layer is increased indicates that the two are connected, and suggests that repeated twinning is occurring in layers parallel to *AB*. Moreover, since the lines appear to

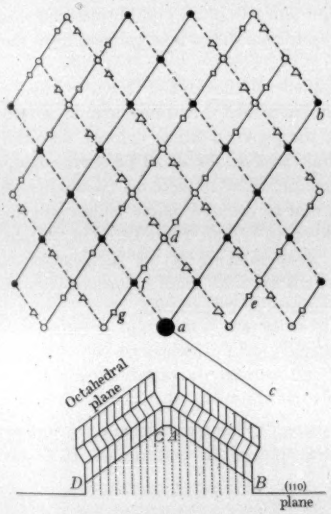

Figure 1.

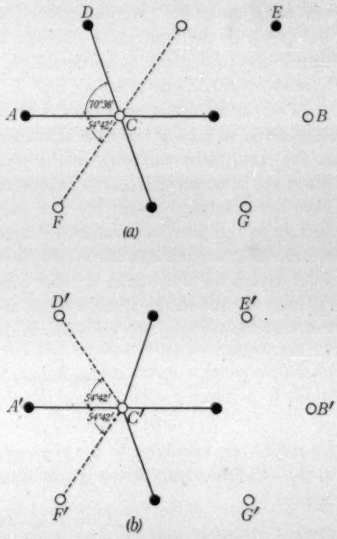

Figure 2.

increase in intensity slightly more quickly than the twin spots and since the twin spots become somewhat drawn out, it is evident that the successive twinning layers are becoming thinner as the thickness of the deposit is increased. Similar considerations apply to the pattern of dotted lines. It is not at first clear why the twin planes should act alone and not simply contribute to the spot patterns. If, however, the equilibrium of atoms in the twin plane is considered, it is seen that they differ from atoms in the interior of a face-centred cubic lattice. Normally a given atom in the lattice has twelve nearest neighbours surrounding it, lying uniformly distributed on a sphere with the given atom as centre. But an atom in the twin plane is not uniformly surrounded by its nearest neighbours. This is seen in figure 2 (*a*), which shows a (111) plane *AB* seen edgeways, i.e. looked at along

a diagonal of a face of the cube. The circles are to be regarded as representing atoms in the plane of the paper and the black spots as atoms in planes immediately above and below the plane of the paper. DE and FG are (111) planes on either side of AB in an ordinary face-centred lattice. It is important to note that a black circle represents two atoms but a white circle only represents one atom, in figure 2.

In figure 2 (*b*), the (111) plane $A'B'$ is seen acting as a twin plane. The asymmetrical position of the atom C' in the twin plane $A'B'$ is immediately seen on comparing its position with that of the atom C in the normal lattice. The atom C' has six nearest neighbours lying to the right and only four to the left. The remaining two neighbours of C' are immediately above and below it. The result must be that the atoms in the twin plane undergo a slight shift to attain equilibrium and this causes the twin plane to be detached, as regards its diffraction pattern, from the lattices on either side of it.

The pattern obtained when the beam is parallel to the edge of the cube must be considered as arising from the structure deduced above. The beam is now parallel to the (110) plane and lying in the plane of the paper in figure 1, lower diagram. Since the successive layers on the octahedral faces of the small projecting lump have been deduced to be very thin (only just sufficient to yield an extended spot pattern in the previous azimuth) it appears that in the new azimuth they will act merely as cross gratings inclined at an angle of 35° 18′ to the beam. The pattern from layers on AB, figure 1, will consist of spots lying at the intersection of (1) lines normal to the shadow-edge, and (2) ellipses with their major axes normal to the shadow-edge. The equation to these ellipses is of the form

$$\frac{\xi^2}{\frac{B^2-AC}{A}}+\frac{(\zeta-B/A)^2}{\frac{B^2-AC}{A^2}}=1.$$

$O\xi$ and $O\zeta$ are axes lying in the plane of the plate, $O\xi$ being parallel and $O\zeta$ normal to the shadow-edge. The origin is the central spot of the pattern. A, B, C are defined by

$$A=\cos^2\alpha_0-\tan^2\alpha\sin^2\alpha_0,$$

$$B=L\sin\alpha_0\cos\alpha_0(1+\tan^2\alpha),$$

$$C=L^2(\sin^2\alpha_0-\tan^2\alpha\cos^2\alpha_0),$$

with $$\frac{\sqrt{6}}{2}a(\cos\alpha_0-\cos\alpha)=n\lambda, \qquad n=0, \pm 1, \pm 2, \text{ etc.}$$

where a is the lattice constant 3·6 A., $\alpha_0 \fallingdotseq 35° 18'$, L is the camera-length 28 cm., and λ is the wave-length 0·061 A. of the electrons. The radius of curvature at the end of the major axis (i.e. in the region actually seen on the plate) is $\sqrt{(B^2-AC)}$. When $n=0$ this gives 19·82 cm. but the zero order cannot be observed. Taking n equal to -2 results in the most suitable ellipse for comparison. The value of the radius when $n=-2$ is 15·4 cm. When an arc of a circle of this radius is drawn on tracing cloth, an excellent fit is obtained with the appropriate spots on the pattern, figure 7. The layers on DC, figure 1, will yield ellipses turned the opposite way.

The interference conditions of the layers on *DC* and on *AB* arising from rows of atoms normal to the beam and parallel to the shadow-edge are expressed by lines normal to the shadow-edge, and these are identical with one another and with the corresponding condition for the original copper. Thus the original side-spacing* is preserved but otherwise the pattern is quite different from that of the original copper. In figure 1, lower diagram, is shown diagrammatically the nickel deposit. The dotted-line shading indicates copper and the full-line shading nickel. Three layers of nickel are shown on each octahedral face, the middle layer being a twin.

Kirchner and Lassen's explanation of the phenomenon of irrational spots—namely, that the (111) planes, being most densely packed with atoms, act as cross gratings—does not appear to be tenable for, on this assumption, irrational spots would be expected in the patterns obtained from ordinary etched specimens of single crystal. The absence of the irrational spots in such cases suggests that they are associated only with deposited layers and that their explanation must be found in the disposition of the layers by the assumption of repeated twinning as indicated above.

Finally will be considered the question of the lattice constant of nickel deposited slowly on the etched copper single crystal. The normal value for nickel is 3·517 A. and for copper 3·608 A. Thus a film of nickel about 100 A. thick should give rise to a pattern of spots close to, but distinct from, the copper spots. No such doubling was observed. Actual measurements on six plates gave the value $3{\cdot}60 \pm 0{\cdot}006$ A., subject to a further uncertainty of about 0·5 per cent due to possible inaccuracies in measurement of camera-length, making the final result $3{\cdot}60 \pm 0{\cdot}03$ A. This is definitely in excess of the value for nickel but equal to that for copper within the errors of experiment. Thus it appears that the nickel, when it is deposited slowly, retains the lattice constant of the underlying copper. This expansion of the nickel lattice may be the cause of the twinning which is observed.

§ 4. COPPER ON COPPER CRYSTAL

Experiments performed. (i) A film of copper 6000 A. thick was deposited at a current-density of 0·75 mA./cm.^{2} The electron-diffraction patterns showed no change from the original copper single-crystal pattern. (ii) A film of copper 20,000 A. thick was deposited at 3 mA./cm.^{2} The same result was found as in case (i). In addition, it was observed that the spots were drawn out towards the shadow-edge. This effect was more pronounced when the thickness was increased to 40,000 A. Also, when the time of deposition had been long, fainter spots were seen, forming the same type of pattern as the copper spots but corresponding to a larger lattice constant than copper. These are evidently the spots obtained by Prof. Thomson[a] and explained by him as due to a copper compound such as Cu_2O. (iii) A film of copper 7500 A. thick was deposited at a current-density of 0·5 A./cm.^{2} The resulting pattern consisted of rings due to ordinary polycrystalline copper.

* By *side-spacing* is meant the spacing of planes normal to the shadow-edge and parallel to the beam of incident electrons.

Explanation of results. It appears from (i) and (ii) that when copper is deposited on the etched face of a copper single crystal at current-densities of 3 mA./cm.^{2} or less, the layer of deposited copper is oriented in exactly the same manner as the underlying single crystal. Also, when the thickness of the deposit is 20,000 A. or more, the diffraction spots are elongated towards the shadow-edge, indicating that refraction is taking place. Thus it may be deduced that the surface has become somewhat flat,* the flat portions being all parallel to the plane free surface of the crystal which is being examined. When the copper is deposited at 0·5 A./cm.^{2} there is no orientation and the deposit has the usual polycrystalline structure.

§ 5. ZINC ON COPPER CRYSTAL

Experiments and results. Deposits of zinc of various thicknesses were obtained with current-densities from 8 μA./cm.^{2} to 1 mA./cm.^{2} In all cases the diffraction pattern was due to ordinary polycrystalline zinc. At the low current-densities the diffraction patterns obtained from the deposits showed the effect of large grain-size.

§ 6. CADMIUM ON COPPER CRYSTAL

Experiments and results. As in the case of zinc the deposits all gave patterns of rings due to polycrystalline metal, even at low current-densities (30 μA./cm.^{2}).

§ 7. SILVER ON COPPER CRYSTAL

Experiments performed. Both (111) and (110) etched faces of the copper single crystal were used. (i) Silver was deposited for 18 hours at 15 μA./cm.^{2} The pattern showed both the original copper spots and spots due to silver. While the copper spots were sharp, the silver spots were really short arcs about 2 mm. long. There were also faint rings due to silver and these passed through the appropriate silver spots. (ii) Silver was deposited for periods of 34, 51 and 72 hours, at the above current density. The same features were observed as in (i), the copper spots becoming very faint with increasing thickness and the rings (due to polycrystalline silver) observed in (i) also became fainter. (iii) When silver had been deposited for 100 hours at 15 μA./cm.^{2} the pattern of spots was entirely due to silver and the silver rings were very faint. In the particular azimuth of the (110) face where the beam is parallel to the cube-edge there were observed, in the pattern, bands running parallel and normal to the shadow-edge and passing through the spots, figure 11. (iv) With a much stronger solution a quick deposit of silver was obtained by simple dipping. This gave a pattern showing rings due to silver and also to copper spots.

Explanation of results. From the above experiments it is seen that, when silver is deposited slowly on the etched copper single crystal, the silver takes the orientation of the copper crystal and gives a similar electron-diffraction pattern except that the normal lattice spacing of silver is retained. The explanation of the thick lines or bands in the pattern observed with a very thick deposit may perhaps be found by

* See reference (9), especially page 647 and figure 2.

analogy with the optical effects obtained with cross gratings. When the number of scattering centres in an optical cross grating is reduced, subsidiary maxima appear in the diffraction pattern and these are not always found to be resolved. Thus they may give rise in the diffraction pattern to lines joining up the spots and of the same breadth as the spots. If the projections through which the electron beam passes were very small (i.e. from 5 to 10 atoms across) then we should expect the electron-diffraction pattern to show these effects; larger projections would give subsidiary maxima too faint to be visible.

When silver is deposited rapidly on the copper crystal there is no orientation and only the ordinary polycrystalline rings are observed.

§ 8. CHROMIUM ON COPPER CRYSTAL

Experiments performed. No deposits were obtained at low current-densities such as had been used in depositing other metals. The plating took place rapidly at high current-densities and was accompanied by vigorous evolution of gas at the cathode. The (111) copper face was used. (i) Chromium was deposited at 0·2 A./cm.^{2} for 20 min. The pattern showed rings due to ordinary polycrystalline chromium. (ii) Chromium was deposited at 0·06 A./cm.^{2} for periods of time ranging from $\frac{1}{3}$ sec. to 20 sec. The patterns showed spots, some sharp, others on the same plate slightly drawn out into arcs. The pattern appeared in its most simple form when the beam

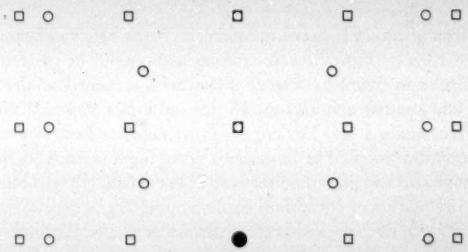

Figure 3.

was approximately parallel to the cube-face diagonal of the copper. The pattern then obtained, figure 10, showed two chromium azimuths simultaneously. This is illustrated in figure 3, where the spots from one azimuth are shown as circles and from the other as squares. (iii) Chromium was deposited at 0·06 A./cm.^{2} for 80 sec. The patterns showed spots as in (ii) and rings passing through the spots. (iv) Chromium was deposited at 0·2 A./cm.^{2} for $\frac{1}{3}$ sec. The results were the same as in (ii).

Explanation of results. A thick layer of chromium on the copper crystal exhibits no orientation and has the ordinary structure of chromium. In the case of thin layers the patterns show at once that there is orientation with (110) planes of chromium, parallel to the (111) copper face, on which the deposit was made. The

spacing of (110) chromium planes only differs by 2 per cent from that of (111) copper planes so that the spots on the centre line due to the chromium and underlying copper must be almost superimposed. There was no doubt, however, that the spots were due to chromium and not copper only, as the side-spacings were quite different from the copper side-spacings. In order to explain why the two chromium patterns occur simultaneously, figure 3, we must examine the azimuths which give rise to these. In figure 4 (*b*) and 4 (*c*) are shown chromium (110) planes. If the electron beam is parallel to *CD*, figure 4 (*b*), we have the $\sqrt{2}$ side-spacing and

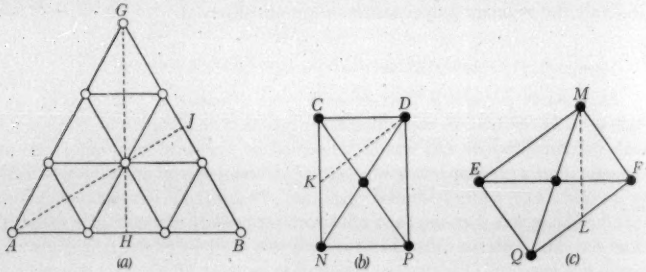

Figure 4.

obtain the pattern of squares shown in figure 3. If the electron beam is parallel to *EF*, figure 4 (*c*), then we have $\sqrt{6}$ side-spacing and obtain the pattern of rectangles indicated by circles in figure 3. Figure 4 has been arranged so that *CD* and *EF* are parallel to one another and also to *AB*, the cube-face diagonal direction of the copper (111) face, figure 4 (*a*). The copper (111) face has been drawn to the same scale as the chromium faces. The chromium (110) faces (*b*) and (*c*) must therefore be imagined moved up and placed on the copper (111) face (*a*), without any rotation. This gives the orientation of chromium on the copper single crystal, with the cube-edge or cube-diagonal of (110) chromium planes parallel to the cube-face diagonal in the (111) copper plane.

§ 9. COBALT ON COPPER CRYSTAL

Experiments performed. The (110) etched face of the copper crystal was used as base. (i) Cobalt was deposited at 4 μA./cm^2 giving thicknesses of deposited metal of 8000, 16,000 and 24,000 A. as calculated by Faraday's laws of electrolysis. The patterns obtained all showed the same features. They were similar to those obtained from the copper crystal alone, but each copper spot in the pattern was replaced by two or four irrational spots according as the electron beam was parallel to (*a*) the cube-face diagonal or (*b*) the cube-edge. In the former azimuth (*a*) each spot was replaced by two spots on either side of it, figure 8. In the latter (*b*) each spot was replaced by two spots, one above and one below, and also by two spots, one on

either side; the sideways separation in this case was much smaller than the vertical separation, figure 9. (ii) Cobalt was deposited at 50 mA./cm.^{2} for a few seconds. Rings due apparently to hexagonal and face-centred cubic cobalt were obtained. Some of the rings due to hexagonal (close-packed) cobalt were not found, but owing to the closeness of several of the lattice spacings this was not considered to cast any doubt on the deduction.

Explanation of results. The irrational spots obtained with cobalt deposits on the copper crystal are similar in some ways to those discussed by Kirchner and Lassen [7]. In all cases the distances between associated irrational spots was greater towards the edge of the pattern than near the central spot, there being a continuous increase in the separation. The explanation must be similar to that laid down for nickel on the (110) copper face, except that additional octahedral planes must be called into

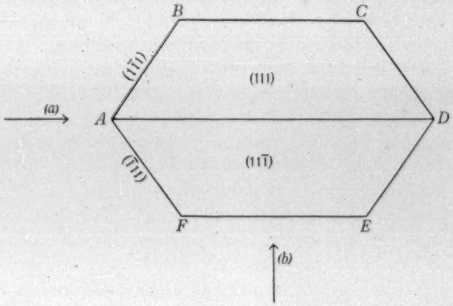

Figure 5.

account besides the two, (111) and (11$\bar{1}$), which were introduced in the discussion on nickel. We may suppose that the (1$\bar{1}$1) and ($\bar{1}$11) planes are also found as bounding faces of a small projection on the copper surface. These planes are normal to the (110) plane and would thus appear as steep vertical sides to the lump or projection considered, whereas the other octahedral planes make an angle of 35° 18′ with the (110) plane. It is not clear why cobalt should be deposited differently from nickel, although it may be noted that the lattice spacings of cobalt and copper are closer than those of nickel and copper. Let us consider a small projection of this nature shown in plan in figure 5, in which the planes *ABCD*, *AFED* are those denoted by *AB*, *CD* in figure 1. It is clear that in azimuth (*a*) only two sets of octahedral layers will be effective, viz. those on *AB* and *AF*, while in azimuth (*b*) there will be four effective octahedral layers, those on *AF*, *AB*, *AFED* and *ABCD*. This accounts for the splitting of the spots which was observed. The production of thin layers may again be attributed to twinning, for in some plates taken in azimuth (*a*) the lines and additional spots obtained with nickel were seen faintly towards the outside of the pattern. Usually, however, they will be obstructed in some way by layers on *AF*, *AB*, *CD* and *DE*.

§ 10. DISCUSSION OF RESULTS

The experiments indicate that metals with a cubic structure may be oriented as single crystals when deposited on the etched copper crystal. The current-density of deposition must not, however, exceed a certain value, otherwise only polycrystalline metal is obtained. This limiting value depends on the metal deposited. Thus copper deposited on the copper crystal at 0·3 mA./cm.^{2} gave a single-crystal pattern, but nickel deposited at this current-density was polycrystalline. Even at very low current-densities, such as 15 μA./cm.^{2}, silver deposits showed some rings due to polycrystalline metal. Hence the closer the agreement between the lattice constants of the deposit and the base, the higher is the limit of current-density for orientation.

Zinc and cadmium, which form close-packed hexagonal lattices but have not the theoretical axial ratio for perfectly close packing, do not appear to be oriented on the copper crystal, at least under the conditions used here.

The metals nickel and cobalt have lattice constants very close to that of copper and it is not surprising that thin layers of them should be deposited exactly like the copper crystal base and with the lattice constant of copper.

The silver deposits differ from those of nickel and cobalt in that the silver has its usual lattice dimensions. Thus the silver atoms cannot be considered as placed one by one immediately above the atoms of the copper base. Nevertheless the *angle* between two intersecting lattice planes of the silver lattice will be exactly the same as the angle between the two corresponding planes of copper. A projection on the surface of the copper crystal may be regarded as bounded by (111) planes, and to a lesser extent by (110) planes and by a few others including (100) planes[10]. This is verified to some extent by examination of the etched crystal using Bridgman's sphere method[11]. If, now, silver atoms are first placed along the edge between (111) and (110) copper planes and then the silver grows over these two copper planes from the edge considered, orientation of the silver as a single crystal will result. The orientation is not uniquely determined since this kind of growth might, for example, give rise to a (111) silver plane on (111) copper or a (111) silver plane on (110) copper. The similarity of arrangement of atoms in the (111) planes of silver and copper may be expected to have some slight effect also in producing orientation and this will produce the observed orientation of the silver on the copper crystal. Other explanations of the manner of deposition might be given, for example, in terms of growing-places. It is only desired here to record the two factors which could determine the orientation: (1) angular fit between a pair of lattice planes in the deposit and a pair of planes of the base; and (2) similar arrangement of atoms in contacting planes.

The orientation of chromium can be considered from the above point of view. Referring to figure 4, it may be shown that the (111) copper plane *GAB* is intersected at right angles along the line *AJ* by a (110) copper plane and by another (110) along *GH*. Again the (110) chromium plane *CDNP* is intersected at right angles along the line *KD* by a (111) chromium plane, where *K* is the mid-point

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

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of *CN*. Similarly, *EMFQ* is intersected at right angles by a (111) chromium plane along *ML*. The figure shows that *KD* is approximately parallel to *AJ*, and *ML* approximately parallel to *GH*. Now the positions of the chromium planes shown in figure 4 can only be regarded as correct to a few degrees because any etched crystal will continue to give the same diffraction pattern when it is turned slightly in azimuth from a given important azimuthal position. Thus there is a strong probability of an exact fit in angle between the chromium (110) and (111) planes and the copper (111) and (110) planes. The copper (111) planes are most extensive and the similarity of arrangement of the atoms in the (111) copper and the (110) chromium planes may decide the orientation observed.

§ 11. ACKNOWLEDGMENTS

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THE MASS OF A CONVECTED FIELD AND EINSTEIN'S MASS-ENERGY LAW

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ABSTRACT. Certain discrepancies between the results of the usual mode of calculating the mass (more particularly the electromagnetic mass) of a charged conductor and Einstein's mass-energy law are discussed and explained.

Einstein's law is contained in the now familiar statement

$$Energy = mass \times c^2 \qquad \ldots\ldots(1),$$

in which c is the velocity of electromagnetic waves in empty space. This statement simply identifies mass and energy. Indeed a trivial change in the definition of energy as something which is measured by work done would enable us to write Einstein's law in the form

$$Energy = mass \qquad \ldots\ldots(2).$$

I am only concerned with cases where a velocity of transport, $\mathbf{v}$, can be assigned to the energy, and the purpose of this communication is to discuss, and to suggest an explanation for, certain discrepancies between the results of the usual mode of calculating the mass—more particularly the electromagnetic mass—of a charged conductor and Einstein's mass-energy law. The electromagnetic contribution m to the mass of a charged spherical conductor which is moving slowly through empty space is usually taken to be given by

$$m = 2e^2/3c^2R \qquad \ldots\ldots(3),$$

where e is the charge in ordinary electrostatic units and R is the radius of the sphere. A very simple calculation convinces us that the energy of the electrical field associated with the charge is

$$e^2/2R \qquad \ldots\ldots(4),$$

and Einstein's law obviously requires that the associated mass m shall be given by

$$m = e^2/2c^2R \qquad \ldots\ldots(5).$$

The expression (3) therefore makes the mass 4/3 times that required by Einstein's law.

When we carry out the calculation by applying the special theory of relativity we get for the electromagnetic contribution to the mass of the charged sphere the expression

$$2\gamma e^2/3c^2R \qquad \ldots\ldots(6)$$

in ordinary electrostatic units, where γ is the factor

$$(1-v^2/c^2)^{-\frac{1}{2}} \qquad \text{.....(7)},$$

provided we carry out the calculation in what I believe is the usual way, namely by calculating the total electromagnetic momentum and assuming the momentum per unit volume to be

$$\mathbf{p}/c^2 \qquad \text{.....(8)},$$

where $\mathbf{p}$ is Poynting's vector.

The theory of relativity however enables us to carry out an analogous calculation for the rest of the mass and this yields the expression

$$\gamma\{E'/c^2 - e^2/6c^2R\} \qquad \text{.....(9)},$$

where E' means the energy of the sphere, exclusive of the electromagnetic part, when at rest. The second term in equation (9) has its origin in the elastic tension due to the surrounding field.

When we add together equations (6) and (9) to get the *total* mass of the charged spherical conductor we find it to be

$$\gamma(2e^2/3c^2R - e^2/6c^2R + E'/c^2),$$

or

$$\gamma(e^2/2c^2R + E'/c^2),$$

which may be written

$$\gamma E/c^2 \qquad \text{.....(10)},$$

where E means the total energy, both electromagnetic and non-electromagnetic, of the sphere when at rest; so that the calculation of the *total* mass yields a result which is in conformity with Einstein's mass-energy law and the law expressing the dependence of mass on velocity.

The discrepancy, which only appears when we deal with the electromagnetic field alone or with the stress-tensor field within the conductor alone, or more generally when the calculation is extended over some limited portion of the region in which the energy is located, is intimately bound up, as we shall see, with the character of Poynting's vector and its analogue in an elastic stress-momentum field. It is well known that Poynting's vector cannot in general be identified with the vector which expresses the energy passing through the unit area per unit time. All that can be said about Poynting's vector, in general, is that its integral over a closed surface correctly expresses the rate at which energy flows from within outwards and it may be replaced in Poynting's theorem by any one of the infinite number of vectors that have the same divergence. In the case of the charged conductor and its convected field, for example, Poynting's vector has not even the same direction everywhere as that in which the energy is travelling and it actually vanishes in some places where there is a very appreciable transport of energy.

Without entering into the details of a calculation which is sufficiently well known it will be helpful to indicate how it comes about that the momentum $\mathbf{M}$ per unit volume in an electromagnetic field in empty space is commonly identified with $\mathbf{p}/c^2$. The x component f_x of the force per unit volume, i.e. the force on the charge in the unit volume, may be (quite correctly) expressed in the form

$$f_x = \frac{\partial t_x^{\,x}}{\partial x} + \frac{\partial t_x^{\,y}}{\partial y} + \frac{\partial t_x^{\,z}}{\partial z} + \frac{\partial t_x^{\,w}}{\partial w} \qquad \text{.....(11)},$$

where x, y and z are rectangular co-ordinates, $w=\sqrt{(-1)}\,ct=ict$, t being the time and $t_x{}^x$, $t_x{}^y$, $t_x{}^z$, $t_x{}^w$ are components of the *stress-momentum* tensor. In fact $t_x{}^x$, $t_x{}^y$, and $t_x{}^z$ are components of the familiar Maxwell stress tensor. The fourth term in (11) may be written

$$-\frac{\partial}{\partial t}\left(-\frac{t_x{}^w}{ic}\right) \qquad \ldots\ldots(12),$$

so that it is perhaps natural—but not necessarily correct, since we may add to $t_x{}^w/ic$ any function of x, y and z without affecting the partial differential quotient (12)—to identify the x component M_x of the momentum per unit volume with $-t_x{}^w/ic$, i.e.

$$M_x=-t_x{}^w/ic \qquad \ldots\ldots(13).$$

We have expressions like (11) for f_y and f_z and a fourth equation

$$f_w=\frac{\partial t_w{}^x}{\partial x}+\frac{\partial t_w{}^y}{\partial y}+\frac{\partial t_w{}^z}{\partial z}+\frac{\partial t_w{}^w}{\partial w} \qquad \ldots\ldots(14).$$

This last equation is simply Poynting's theorem. In fact $-icf_w$ is equal to the rate at which work is done on the charge per unit volume at the expense of the field energy, and hence, if

$$p_x=ict_w{}^x \qquad \ldots\ldots(15),$$

p_x is the x component of Poynting's vector. The tensor $\mathbf{t}$ is symmetrical, i.e.

$$t_x{}^w=t_w{}^x,$$

so that we get from (13) and (15)

$$-icM_x=p_x/ic,$$

or

$$M_x=p_x/c^2 \qquad \ldots\ldots(16).$$

Poynting's vector $\mathbf{p}$ is, of course, in the units used in this paper (that is, ordinary electrostatic units for electrical quantities and ordinary electromagnetic units for magnetic quantities) expressed by

$$p=\frac{c}{4\pi}\,\mathbf{E}\times\mathbf{H} \qquad \ldots\ldots(17),$$

where $\mathbf{E}$ is the electric field-intensity and $\mathbf{H}$ the magnetic field-intensity, and the symbol $\times$ indicates a vector product. The momentum, $\mathbf{M}$, per unit volume of the electromagnetic field, as given by (16), may therefore be expressed by

$$\mathbf{M}=\mathbf{E}\times\mathbf{H}/4\pi c \qquad \ldots\ldots(18).$$

The calculation of $\mathbf{E}$ and $\mathbf{H}$ in equation (18) for the case of a charged sphere is easily effected by using the Lorentz transformation. We start with co-ordinates x', y', z' in which the sphere of radius R is at rest. The electric field-intensity at any point distant r from the centre is

$$\mathbf{E}'=e/r^2,$$

while the magnetic field-intensity $\mathbf{H}'$ is zero. We then transform to axes x, y, z which are in motion in the common x' or x direction with the constant velocity $\mathbf{v}$. We thus find for M_x, the x component of the momentum per unit volume, at a point in the electromagnetic field the expression

$$M_x=\gamma^2\mathbf{v}\,e^2\sin^2\theta/4\pi c^2r^4 \qquad \ldots\ldots(19),$$

where r is the radial distance of the point from the centre of the sphere, measured in the co-ordinates in which the sphere is at rest, and θ is the angle between the radial line and the x' axis. We multiply this by the volume element

$$r^2 dr \sin\theta \, d\theta \, d\phi/\gamma,$$

and integrate over the whole electromagnetic field. The division by γ must be made because r, θ and ϕ are polar co-ordinates in the system in which the sphere is at rest. We thus get for the total momentum due to the electromagnetic field the expression

$$\gamma \{2e^2/3c^2R\} \mathbf{v} \qquad \text{.....(20).}$$

The calculation of the momentum of the interior of the charged sphere is very similar. The stress-momentum tensor, referred to co-ordinates x', y', z', w' in which the sphere is at rest, has only the four following components which do not vanish:

$$\left.\begin{aligned} t'_x{}^x = t'_y{}^y = t'_z{}^z = e^2/8\pi R^4 \\ \text{and} \qquad t'_w{}^w = U', \text{ the energy per unit volume} \end{aligned}\right\} \qquad \text{.....(21).}$$

On applying the appropriate equations of transformation to obtain the components of this tensor in the co-ordinate system in which the charged body is in motion with the velocity $\mathbf{v}$ in the x direction, we find

$$t_x{}^w = \frac{\gamma^2 v}{ic} \{t'_w{}^w - t'_x{}^x\}$$

or

$$t_x{}^w = \frac{\gamma^2 v}{ic} \{U' - e^2/8\pi R^4\},$$

and thus obtain for the x component of the momentum per unit volume

$$M_x = -t_x{}^w/ic = \frac{\gamma^2 v}{c^2} \{U' - e^2/8\pi R^4\},$$

and hence for the whole of the interior momentum, on multiplying by the volume $4\pi R^3/3\gamma$,

$$\gamma \{E' - e^2/6R\} \mathbf{v} \qquad \text{.....(22).}$$

The fact that the calculations outlined above yield a result for the *total* mass and momentum which accords with Einstein's law, while they yield results for the mass and momentum of some *part* of the field which are generally in conflict with Einstein's law, can be explained in the following way.

If U be the energy per unit volume at *any* point in the field (whether in the electromagnetic field outside the charged conductor or in the elastic stress-tensor field within it) the associated mass is undoubtedly U/c^2, so that

$$\rho' = U/c^2 \qquad \text{.....(23),}$$

where ρ' means mass per unit volume. The momentum per unit volume will be expressed by

$$\mathbf{M}' = U\mathbf{v}/c^2 \qquad \text{.....(24).}$$

This, it should be noticed, is a correct expression for the momentum per unit

volume and differs from that expressed by equation (18), for example, since at a point in the electromagnetic field equation (24) is equivalent to

$$\mathbf{M}' = (\mathbf{E}^2 + \mathbf{H}^2)\,\mathbf{v}/8\pi c^2.$$

The correct expression for the energy-transport vector is clearly

$$\mathbf{p}' = U\mathbf{v} \qquad \text{.....(25)},$$

so that

$$\mathbf{M}' = \mathbf{p}'/c^2 \qquad \text{.....(26)}.$$

If now we base the calculation of mass on equation (23) and the following equations we are bound to get correct results whether we deal with the whole or merely with a part of the field. The calculation of the total mass might be effected in the following way. We imagine a closed surface which includes a volume so large that all the energy—or all except an infinitesimal fraction—is within it at some instant t, and that all the energy has passed out of it during an interval of time τ, in consequence of the convection with the velocity $\mathbf{v}$. The total mass will then be expressed by

$$\text{Mass} = \int_t^{t+\tau} dt \iint \mathbf{M}' . \mathbf{dS} \qquad \text{.....(27)},$$

where $\mathbf{dS}$ is a surface element and also a vector which is directed outwards and $\mathbf{M}' . \mathbf{dS}$ is a scalar product. The double symbol $\iint$ represents an integration over the whole of the closed surface. Finally, on making use of equation (26) we get

$$\text{Mass} = \frac{1}{c^2} \int_t^{t+\tau} dt \iint \mathbf{p}' . \mathbf{dS} \qquad \text{.....(28)}.$$

If now in this equation we were to replace $\mathbf{p}'$, which is the true energy-transport vector, by Poynting's vector $\mathbf{p}$ (or its analogue in the elastic stress-tensor field) we should get a correct result, that is a result in agreement with equation (10) for the total mass, as we shall show The difference between the two modes of calculation is due to using the faulty expression (16) for momentum-density in one case and the correct one (26) in the other. Now it is a property of Poynting's vector (and of its analogue) that the surface integral $\iint \mathbf{p} . \mathbf{dS}$ correctly expresses the rate of flow of energy through the closed surface from within outwards, notwithstanding the fact that $\mathbf{p}$ does not in general express the transport of energy through the unit area per unit time. Therefore

$$\iint \mathbf{p}' . \mathbf{dS} = \iint \mathbf{p} . \mathbf{dS},$$

and we have an explanation of the fact that we get a correct expression for the total mass while using a faulty expression for the momentum-density.

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THE PARAMAGNETISM OF THE RARE-EARTH SULPHATES AT LOW TEMPERATURES

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ABSTRACT. The magnetic susceptibilities of powdered specimens of the octahydrated sulphates of ytterbium, dysprosium and erbium have been measured from room temperature down to 14° K. The results are discussed in terms of the crystalline-field theory of Penney and Schlapp. Measurements on $Nd_2(SO_4)_3.8H_2O$ support the observations of Gorter and de Haas as against those of Selwood.

§ 1. INTRODUCTION

THE measurements made by Gorter and de Haas[1] in the temperature range 290° to 14° K. of the magnetic susceptibilities of the octahydrated salts of praseodymium and neodymium showed that those salts obey the law

$$\chi(T+\Delta)=\text{a constant}$$

at the higher temperatures. Deviations however set in as the temperature falls, the susceptibility of the praseodymium salt increasing *less* rapidly with decrease in temperature and becoming almost independent of T below 20° K., while that of the neodymium salt increases more rapidly with decrease in T than is given by the above formula. These strikingly different behaviours have been shown by Penney and Schlapp[2] to be explicable on the same theoretical basis. The paramagnetic ion is assumed to be situated in an inhomogeneous electrostatic field of appropriate symmetry and strength. Each of the energy levels of the free ion is split in this crystalline field into a number of levels, the separations between which are small compared with the distances between the levels of the free ion in the case of the rare-earth salts.

The variation with temperature of the population of these sub-levels then gives rise to the deviations from the Curie law, $\chi T=$ a constant, observed with these salts. The different behaviour of praseodymium and neodymium salts is due to the difference in the effect of the same crystalline field on ions containing an even and an odd number of electrons respectively.

By a suitable choice of the strength of a field of cubic symmetry, Penney and Schlapp were able to reproduce the experimental results in a very satisfactory way and to deduce the situations of the energy levels of the paramagnetic ions in the crystals.

Now since all the rare earths, with the possible exception of cerium, give octahydrated sulphates and since the crystalline fields of all these salts may be expected to be very similar in strength and symmetry, it would appear to be of considerable interest to extend the measurements to as many of the other rare earths as possible. The applicability of the crystalline-field theory could be further tested and in the event of its success the energy levels of the various paramagnetic ions in the crystals could be determined. With this end in view a series of measurements has been commenced in this laboratory on material of very high and accurately known purity over the temperature range 290–14° K.

The present paper deals with the observations on the sulphates of ytterbium, dysprosium and erbium. In addition, the susceptibility of neodymium sulphate has been investigated with the object of deciding whether the results of Gorter and de Haas or the more recent ones of Selwood[3] are the more nearly correct.

§ 2. EXPERIMENTAL RESULTS

The susceptibilities of powdered specimens of the rare-earth sulphates were determined over the range of temperature 290–14° K. by means of the Sucksmith magnetic balance adapted for use at low temperatures as described in a previous paper[4]. The low temperatures were obtained with the aid of baths of liquid ethylene, oxygen, nitrogen and hydrogen boiling under suitable pressures, together with solid carbon dioxide and acetone. The finely powdered specimens were enclosed in small sealed spherical phials of pyrex glass.

Ytterbium sulphate, $Yb_2(SO_4)_3.8H_2O$. This was prepared from a sample of ytterbium oxide (Lab. No. 8218) supplied by Messrs Adam Hilger. The report of a spectroscopic analysis accompanying the specimen indicated that slight traces of calcium and sodium were present, but barium, cerium, erbium, europium, gadolinium, lanthanum, magnesium, manganese, scandium, strontium, terbium and yttrium were definitely absent.*

The reciprocals of the molecular susceptibilities, corrected for diamagnetism,† are plotted in figure 1, curve I.

It will be seen that ytterbium sulphate obeys the law $\chi(T+\Delta)=$ a constant, with Δ equal to $+42$ down to about 60° K., but that at lower temperatures the susceptibility is greater than is given by the above expression.

This behaviour is to be expected for a magnetically dilute salt containing a rare earth ion with an odd number of electrons.

Dysprosium sulphate, $Dy_2(SO_4)_3.8H_2O$. The specimen used was prepared from the oxide (Lab. No. 6402) supplied by Messrs Adam Hilger. Spectroscopic analysis showed that the sample contained a trace of magnesium and perhaps slight traces of

* When an element is stated to be "absent", the substance under examination does not contain as much as 0·01 per cent of it, except that for praseodymium, the corresponding figure is 0·1 per cent.

† The following values of the gram-molecular susceptibilities have been used in calculating the correction for diamagnetism: $SO_4 = -33{\cdot}4\times10^{-6}$, $H_2O = -13{\cdot}0\times10^{-6}$. No correction has been applied for the diamagnetism of the rare-earth ion in view of the uncertainty of the value to be taken. The correction still to be applied may therefore amount to $\frac{1}{2}$ per cent for Yb^{+++} at room temperature but is negligible for the other ions.

calcium and gadolinium. Cerium, lanthanum, neodymium, samarium and yttrium were absent and praseodymium "probably absent". The corrected reciprocals of the observed susceptibilities are plotted in figure 2, curve I.

Dysprosium sulphate thus follows the law $\chi(T+\Delta)=$ a constant, with Δ equal to about 1·5 down to the lowest temperature investigated.

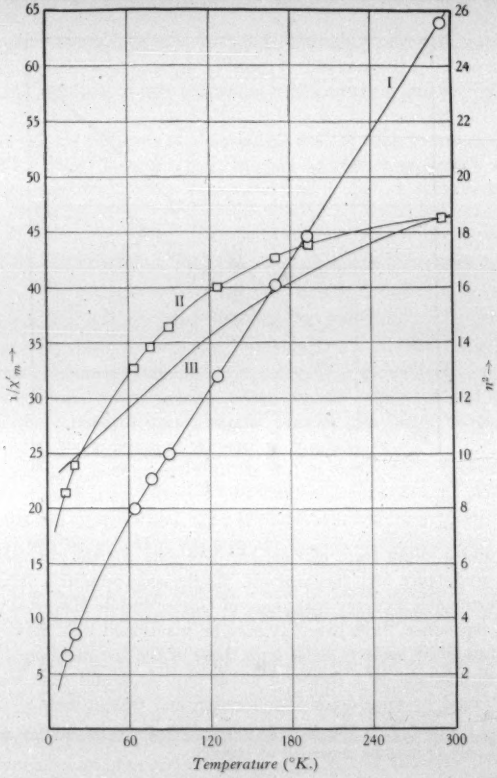

Figure 1.

Erbium sulphate, $Er_2(SO_4)_3.8H_2O$. The specimen was prepared from oxide (Lab. No. 10374) supplied by Messrs Adam Hilger. They report that a spectroscopic examination showed the doubtful presence of a trace of yttrium but no other impurities. The corrected reciprocals of the observed susceptibilities are plotted in figure 2, curve II.

These results fit the formula $\chi(T+6)=$ a constant, down to the lowest temperature investigated.

Neodymium sulphate, $Nd_2(SO_4)_3.8H_2O$. The specimen used was prepared from the oxide (Lab. No. 6783) supplied by Messrs Adam Hilger. The report of a spectroscopic analysis of the sample showed that it contained 0·1 per cent of gadolinium, 0·03 per cent of lanthanum, and 0·1 per cent of samarium, together with a trace of

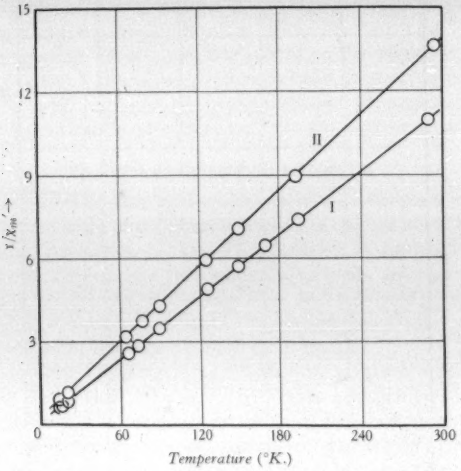

Figure 2.

magnesium and a slight trace of calcium. The data for the susceptibility were corrected in accordance with this analysis. As the susceptibilities obtained agreed within their estimated accuracy with those of Gorter and de Haas it is not thought necessary to reproduce them here. It may be mentioned that Selwood's results for this salt can all be made to agree with those of the last-mentioned workers by multiplying throughout by a factor of about 0·9. It would thus seem that his results are affected by some error of calibration and that in view of their confirmation by the present work the susceptibility data given by Gorter and de Haas for $Nd_2(SO_4)_3.8H_2O$ may be regarded as correct.

§ 3. DISCUSSION OF THE RESULTS

In comparing the experimental results with the predictions of the crystalline-field theory, the susceptibilities are calculated by means of the general expression (1)

$$\chi_m = -\frac{N}{H}\Sigma\frac{\partial W}{\partial H}e^{-W/kT} \div \Sigma e^{-W/kT} \qquad \ldots\ldots(1),$$

in which χ_m is the molecular susceptibility, N the Avogadro number, and W the energies of the various levels in the presence of the magnetic field. The summation is to be made over all the levels which contribute appreciably to the magnetization. In the case of the magnetically dilute compounds of the rare earths, the levels in question except for europium and samarium will be the ones into which the lowest component of the fundamental multiplet (the ground state) is split by the crystalline field.

The energies W have then to be calculated assuming some particular properties of the crystalline field in respect of symmetry. The over-all splitting of the levels depends on the strength of this crystalline field and their number on its type of symmetry.

Ytterbium. In the presence of a crystalline field of cubic symmetry, the lowest state of the Yb^{+++} ion ($J=7/2$) is split into two two-fold degenerate levels and one four-fold degenerate level. When a magnetic field is applied, these levels split into the following eight levels[5]:

$$W_1 = -14a + 1{\cdot}167\,G - 0{\cdot}3240\,G^2/a,$$
$$W_2 = -\ 2a + 1{\cdot}833\,G + 0{\cdot}3240\,G^2/a,$$
$$W_3 = -\ 2a + 0{\cdot}500\,G - 0{\cdot}1500\,G^2/a,$$
$$W_4 = \ \ 18a - 1{\cdot}500\,G + 0{\cdot}1500\,G^2/a,$$

and four more obtained by changing the sign of G. In the above expressions $a=12pD$, where D is a constant expressing strength of the cubic field and p involves an integral of a radial wave function taken over the whole ion and is nearly the same for all the rare-earth ions, $G=g\beta H$, g being the Landé factor, β the Bohr magneton, and H the strength of the applied magnetic field.

Calculations have been made with the aid of the above expressions, and the curve for n^2 (where n is the effective Bohr magneton number $=3\chi'_m kT/N\beta^2$) which passes through the experimental value at room temperature is plotted in figure 1, curve III. It will be seen that the assumption of a crystalline field having cubic symmetry does not reproduce the experimental results (figure 1, curve II) at all accurately. It remains to test whether a field of lower symmetry will give satisfactory agreement or whether other factors have to be taken into account in the explanation.

Dysprosium and erbium. The ground state for the ions of both these elements is split by a crystalline field of cubic symmetry into two two-fold degenerate levels and three four-fold degenerate levels ($J=15/2$). The calculation of the expressions for the levels in the presence of a magnetic field is, however, very complicated for so high a value of J and has not yet been carried out. If, however, it is permissible to estimate the width of the over-all splitting due to the crystalline field in the case in which $J=15/2$ from the known results for those in which $J=7/2$, 4 and $9/2$* it is seen that this over-all splitting for dysprosium and erbium must be at least ten times as great as that for neodymium with the same strength of the electric field. Thus although the positions of the separate levels are unknown, the separation

* 384, 296 and 1823 A. respectively for a field of cubic symmetry such that $A=pD$.

between the lowest and the next highest level will, in the absence of a magnetic field, be 2000 $cm.^{-1}$ or more for the octahydrated sulphates of these two elements. It is thus clear that any levels but the lowest will be practically unoccupied even at room temperature. The magnetic behaviour of these salts will therefore deviate but little from Curie's law in agreement with the experimental observations.

Further consideration of the results shows that this cannot be the correct explanation, for the magneton number deduced from the susceptibilities would be quite different from the Hund value for the free ion, whereas the experimental value for the effective magneton number is almost equal to the Hund value at any temperature above about 60° K. To account for this result and for the small deviation from Curie's law it is necessary to assume that the over-all splitting of the ground state by the crystalline field in these salts is very small, and indeed not more than about 40 $cm.^{-1}$, as against the observed value 834 $cm.^{-1}$ for the corresponding salt of neodymium.

This result is surprising since $Er_2(SO_4)_3.8H_2O$, and presumably also $Dy_2(SO_4)_3.8H_2O$, is isomorphous with $Nd_2(SO_4)_3.8H_2O$ and the molecular volumes of these salts do not differ greatly. It would therefore be expected that the crystalline fields in all three of the salts would be very similar as regards strength and symmetry. It appears, however, that, unless there is some at present unsuspected factor which results in the states of high J-value being much less affected by a cubic crystalline field than those of lower J, the strength of the field in $Dy_2(SO_4)_3.8H_2O$ and $Er_2(SO_4)_3.8H_2O$ is very small.

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535.8:612.84

VISION IN OPTICAL INSTRUMENTS*

By CHARLES FABRY

The Thomas Young Oration, delivered December 6, 1935

§ 1. THOMAS YOUNG

To me it is a great honour to have been invited to give this lecture in honour of Thomas Young.

You will not expect from me a summary of the extremely extensive work of Thomas Young. I should like, however, to remind you of the admiration felt for him by French physicists, even during his own lifetime. He was probably more fully appreciated in France than in his own country. Young had many friends in France, he came several times to Paris, and certain of his French friends went to London for the special purpose of conferring with him, particularly on the theory of light, which was then receiving much attention in France. At the time of Young's death, Arago was the Secretary of the Académie des Sciences, of which Young was of course a foreign member. Now, our Academy holds an annual formal meeting, at which Arago was accustomed to read an "éloge" on some recently deceased scientist whom he had known personally. Naturally, the man to whom he rendered this homage was generally French, and I have only found three exceptions to this rule: James Watt, Alessandro Volta and Thomas Young, and the juxtaposition of these three names shows how Thomas Young was admired.

Young lived in a very brilliant period of French science, with men like Laplace, Lagrange, Fourier, Monge, Ampère, Fresnel, Poisson, Arago and others. The complete understanding of Thomas Young's work in French scientific circles is very remarkable, because of the great difference in their mental outlook. The characteristic feature of French science at this time was its very strong mathematical bias; Young was not ignorant of mathematics (there was probably nothing in which he was ignorant), but mathematics was not his natural language. Laplace expressed this peculiarity by saying that in the work of Thomas Young there were more general surveys than accurate demonstrations. Perhaps in Laplace's mind this opinion implied a certain criticism of Young; we should add that Young's general arguments were those of a great genius, and that the two types of mind, that which leads to general conclusions and that which ends up in a mathematical demonstration, are both necessary to the progress of science.

* Translated by Mr J. H. Awbery.

§ 2. THE PROBLEMS OF VISION

I shall speak of vision in optical instruments, or of the eye considered as a part of every instrument which assists vision. The problems to be solved are the following: what can we *see* in a given optical instrument, and as a correlative question, how must an instrument be constructed to *see* a certain thing? First of all it is necessary that the details which we wish to see should be truly separated by the instrument, but in general this is not sufficient.

Geometrical optics indicates no limit to the resolution in a perfect instrument. This idea is curiously expressed by Descartes in his Dioptrics, published almost exactly three centuries ago, at a time not very distant from the first astronomical discoveries made by Galileo with the telescope. Applying the exact law of refraction to the theory of the telescope for the first time, Descartes discovered what is now called spherical aberration in objectives, and expressed the opinion that this aberration was the sole cause which limited the resolving power of the telescope. He sought therefore what form must be given to the surfaces in order to obtain an exactly stigmatic image, and showed that this result would be reached by means of a lens with one plane face and one in the form of a convex hyperboloid—an easy problem for a present-day student, but difficult enough half a century before Newton. Descartes added that if such a lens were to be made it would enable entirely new things to be seen, such as the inhabitants of the moon. Descartes was so sure of his results that he designed a machine for shaping the hyperbolic surface and spent a certain amount of money, including that of his friends, in building it. We have never heard that he was repaid by seeing the inhabitants of the moon.

Much later, the theory of diffraction permitted the calculation of the effect of a perfect optical instrument, independently of the eye, following the general ideas of Young, the more penetrating theory of Fresnel, the complete calculations of Airy, and Foucault's experimental studies. This theory gives the form of the diffraction pattern in a perfect instrument when forming an image of a luminous point; from it is deduced the limiting separation for a set of two points, such as a double star. The result is as follows: a 5-in. objective can just separate two points with an angular distance of 1 sec., and this limit falls off inversely as the diameter of the objective.

Now it is quite evident that this criterion of resolution does not in general represent what can really be seen. For example, the star Sirius has a companion of the 8th magnitude at a distance of about 8 sec. from the main star. A 2-in. telescope should thus show the satellite easily; actually, I believe that a ten times greater diameter is necessary for seeing it.

Again, the theory of diffraction assumes that the instrument is geometrically perfect. In testing an instrument, it is common to use Foucault's test object, formed of equidistant black lines on a white background, the width of the black lines being equal to that of the transparent intervals. The theory of diffraction gives the limit of the angular interval that can be separated, and an instrument is regarded as good if its resolving power is equal to the theoretical power. Now experience

shows that if the test object is well illuminated, practically all instruments, even the most ordinary, have the theoretical resolving power; nevertheless, the different instruments are far from being equally effective in use, and a simple glance at a landscape gives a more useful indication of the value of the instrument than does an examination by means of Foucault's test object.

On examining how a real object differs from the test object, we find two essential differences: (1) In a landscape, objects are seen which present only a feeble contrast both internally and to the background, whereas Foucault's test object shows complete contrast (black and white); (2) The brightness is not in general within the control of the observer, and may vary within extraordinarily wide limits (for example, from 1 to 10^9).

We must therefore commence by studying the capacity of the eye to grasp details under these various conditions. Moreover, in the majority of instruments, the pupil of the eye is restricted by the exit pupil of the instrument.

We are thus led to study the conditions of vision by the naked eye, introducing the three quantities which follow. (1) *Contrast*. The test object is composed of equal equidistant lines, but instead of presenting a complete contrast, these should exhibit simply a difference in brightness between the "light lines" and the "dark lines". If B and b are the brightnesses of these two parts, the contrast γ is defined as $\gamma=(B-b)/B$. The case of Foucault's object (black lines, $b=0$) corresponds to $\gamma=1$ (complete contrast). The other extreme case is $\gamma=0$ (complete absence of lines). (2) *Brightness*. The brightness of the test object is characterized by the value of B, the brightness of the lightest parts. A unit must be selected for this quantity. Brightness is luminous intensity per unit of area; we shall express it in candles per cm^2, a unit to which M. Blondin has proposed to give the name of *stilb*; this name was recently approved by the International Commission on Illumination. It is rather too large a unit, but this is only of minor importance. To link this up with British units, we may consider a perfectly white object diffusing according to Lambert's law; if it receives illumination E foot-candles, then its brightness in stilbs is

B, b, γ

E

$$B=3{\cdot}43\times10^{-4}E.$$

Values of B greater than 0·01 stilb correspond to well-lighted objects, those less than 10^{-6} to feeble or very feeble illumination, whilst the limit of perception (below which a surface cannot be distinguished from perfect darkness) is about 10^{-10} stilb. (3) *Diameter of pupil utilized*. This will be expressed in millimetres and designated by ω. In an optical instrument this is, most usually, the diameter of the exit pupil. In experiments on the naked eye, it will be an artificial pupil consisting of a small circular aperture in a thin metal plate.

ω

When these three variables are fixed, we may seek the limit of separation,* defined as the least angular distance between the centres of two similar marks at

* The expression "resolving-power" easily gives rise to confusion. This "power" is expressed as the least visible angle; the smaller the angle, the better is the resolution. When we say that the resolving-power is increased, it is difficult to know whether the instrument is better or worse. For this reason I shall speak of "limit of separation".

which they can be distinguished as separate. It will be denoted by s and expressed in minutes of arc.*

The result of this study of the eye will be to determine a function s of three variables, such that

$$s = f(\gamma, B, \omega).$$

The experimental study of a function of three variables is always a long task. The present one has already given rise to numerous investigations, among which I would mention those of Luckiesh and Moss, and that of P. W. Cobb, Danjon, Dufay and Mlle Schwégler. Each of these researches covers only a part of the field of useful variation in γ, B and ω; in particular they do not extend sufficiently far into the region of low brightness and weak contrasts, which is the most interesting for certain applications of optical instruments. I shall refer particularly to the very complete and careful measurements carried out at the Institut d'Optique by M. A. Arnulf, with the co-operation of several workers at the same laboratory;† these measurements have not yet been published.

§ 3. CONSTRUCTION OF TEST OBJECT WITH VARIABLE CONTRAST AND BRIGHTNESS

The object employed is similar to that of Foucault, but with a greater or less contrast between the light lines and the darker ones. To obtain this result, the simple method of the revolving disk has been used. On a white carboard disk concentric black circles are traced, the width of the black bands being equal to the white portion left between two successive black bands. Each black circle extends over a part only of the circumference. When the disk is turned rapidly, only white and grey circles are seen; if the black circles occupy $1/n$ of the circumference, the contrast $\gamma = 1/n$. In the case shown in figure 1, $\gamma = 0{\cdot}5$. There is thus a series of disks, each corresponding to a given value of γ, from $\gamma = 1$ to $\gamma = 0{\cdot}006$. The diameter of the disk is 30 cm.; it is mounted on the shaft of an electric motor which turns it at the rate of 4000 r.p.m.; under these conditions, the surface of the disk is seen without any flickering. A black screen covers part of the disk, leaving a rectangular area visible, figure 1; it is this rectangle which serves as test object.

In order to vary the brightness, it is only necessary to vary the illumination of the disk. For high brightness, the disk is illuminated directly by means of an electric arc, and for less brightness by a tungsten strip lamp; for still less brightness, the arrangement shown in figure 2 is used; L is a tungsten strip lamp, which shines on a diffuser D provided with a variable diaphragm. In order to reduce the brightness further, a neutral filter of known transmission is put at E.‡ In each case, the

* It would be more logical to express it in radians, but the minute as a unit of angle is more familiar.

† I tender my thanks to Mr Arnulf who has allowed me to make use of these results as well as of important theoretical suggestions before publishing them himself.

‡ The Institut d'Optique has an excellent collection of neutral filters, which is a gift of great value from Prof. Tscherning of Copenhagen. These filters are remarkably homogeneous and remarkably neutral, and their transmission factors, which vary from 0·56 to 10^{-10}, are very exactly known. Their use has contributed greatly to facilitate the measurements.

brightness B (that of the light parts of the object) is directly measured by means of Jobin and Yvon's photometer, the measurements being taken on the white parts when the disk is stationary. For the smallest brightnesses, of which the direct measurement would be very uncertain, the measurement is made before inserting the filter, and then applying the accurately known transmission factor.

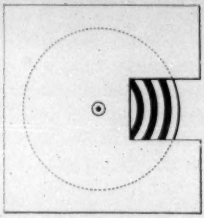

Figure 1.

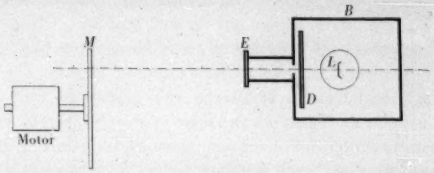

Figure 2.

To obtain various apertures ω of the pupil, a number of accurately circular holes are made in a thin metal sheet which the observer places in front of his eye. The diameters of these openings are measured by means of a comparator.

§4. PROCEDURE IN EXPERIMENTS ON VISION WITH THE NAKED EYE

Each disk gives a definite value of the contrast γ. After a disk has been inserted it is subjected to a definite illumination and therefore has a definite brightness, which is measured. The observer places a pupil of known diameter ω before his eye; he goes in front of the rotating disk, in complete darkness (after an adaptation period which is the longer the less the brilliance), and he finds the maximum distance at which he can still distinguish the marks; from this, the limit of separation s corresponding to the particular values of γ, B and ω is deduced.

The observer changes the pupil (which only means that he looks through a different hole in the metal plate) and resumes the observations, and so on for all the values of ω. The illumination, and consequently the brightness is then changed, and the observer goes through the same series again. Finally the rotating disk is changed, in order to alter γ, and the double series of measurements is repeated.

All the observers were youthful, and had good accommodation and normal vision. Certain observers who had an incurable tendency to regard the experiments as a sort of sporting contest, with the one who could see the marks at the greatest distance as the winner, had to be eliminated. The observations were very lengthy, owing to the necessity of varying three independent variables, especially the brightness, between very wide limits. The experiments are particularly fatiguing at very low brightnesses, where complete darkness and a long adaptation are essential.

§ 5. RESULTS

The results of the measurements are represented on a series of diagrams, each referring to a given value of the brightness. On each diagram, the pupil diameters ω are plotted as abscissae and the limits of separation s as ordinates, each curve referring to a given value of the contrast γ. Figures 3, 4 and 5 show examples of these diagrams for three different values of the brightness, one strong, one medium, and one low.

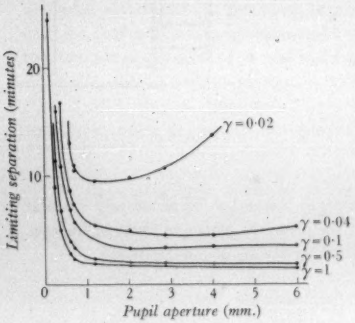

Figure 3. Brightness of the object, 0·148 candles/cm²

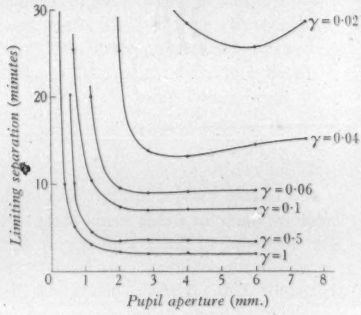

Figure 4. Brightness of the object, $1{\cdot}2 \times 10^{-4}$ candles/cm²

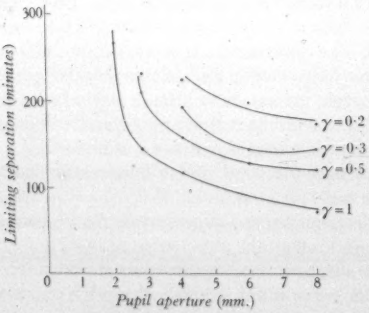

Figure 5. Brightness of the object, $0{\cdot}4 \times 10^{-8}$ candles/cm²

Consider first a high brightness like that encountered in a well-lit landscape; the results are shown in figure 3, for which B is 0·15 stilb (i.e. equal to the brightness of a white diffuser under an illumination of 400 foot-candles). For very good contrast, we have the curve marked $\gamma = 1$; the value of the limit of separation is practically

constant for all sizes of the pupil greater than 1 mm.; this limit only increases as ω becomes very small, and it increases indefinitely as ω approaches zero. For slight contrasts the values of s become much greater, and the curve is altered in shape. The limit of separation passes through a minimum at a certain size of pupil; for example, at the very low contrast $\gamma = 0{\cdot}02$ the minimum of s corresponds approximately to $\omega = 1$ mm., and this minimum of the limit of separation is about 10′, ten times as large as for complete contrast.

If now we consider weaker and weaker brightnesses, down to the limit of perception which lies at about 10^{-10} stilb, we find that all the values of the limit of separation increase considerably, and at the same time the shapes of the curves are altered. Examples of these changes are seen in figures 5 and 6, which correspond to brightnesses of $1{\cdot}2 \times 10^{-4}$ and $0{\cdot}4 \times 10^{-8}$ stilb. The enormous values which the limit of separation can attain will be noticed; whilst values in the neighbourhood of 1′ are found with high brightness and good contrast, yet for low brightness the minimum of s can reach 258′ (i.e. more than 4°). This is why at night black objects can only be seen against the sky if their apparent diameters are considerable.

§ 6. COMPARISON WITH THE THEORY OF DIFFRACTION. SPECIFIC LIMIT OF SEPARATION

These results are in total disagreement with those predicted by the theory of diffraction for a perfect instrument. Moreover, that theory takes no account either of brightness or of contrast; it leads to a simple relation between s and ω, of the form $s\omega = \text{constant}$. The curve would be a hyperbola with the axes as asymptotes. This is approximately verified for a region containing extremely small pupil-sizes in the case of good contrast and high brightness, but not at all for the remainder of the curve.

Mr Arnulf considers the quantity σ equal to $s\omega$. It is convenient in the study of instruments, and he proposes to call it the *specific limit of separation*. This quantity would be a constant if diffraction alone were operative. A series of diagrams can be drawn for σ analogous to those for s. Each diagram refers to one value of the brightness; on each, the pupil diameter ω is taken as abscissa and the specific limit of separation σ (in millimetres × minutes of arc) as ordinate. If diffraction alone acted there would be a single diagram consisting of a horizontal line. Figures 6, 7 and 8 give examples of diagrams obtained for three values of the brightness, viz. $B = 0{\cdot}15$ (high brightness), $B = 1{\cdot}1 \times 10^{-5}$ (low) and $B = 0{\cdot}4 \times 10^{-8}$ (very low).

For high and medium brightnesses (e.g. $B > 10^{-4}$, which corresponds to a white body with an illumination of 0·3 foot-candles), the curve has a straight part, and then a minimum as ω diminishes, finally rising again for very small values of ω. The value $B = 10^{-5}$ is a transition region, a sort of twilight, where the curves are irregular and complicated; it is probably the region where red-sensitivity disappears. At very low brightnesses, as for example that of the night sky on a moonless night, and corresponding to nocturnal vision, the curves become regular again, but now have no minimum; σ decreases steadily as ω diminishes.

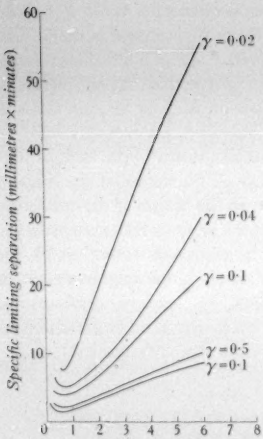

Figure 6. Brightness of the object, 0·15 candles/cm²

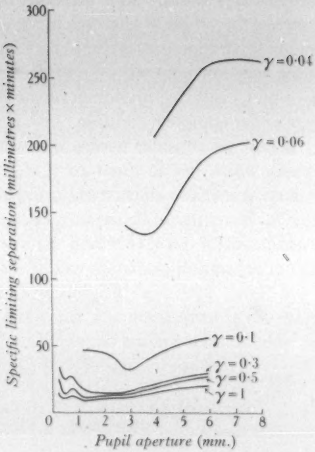

Figure 7. Brightness of the object, $1{\cdot}1 \times 10^{-5}$ candles/cm²

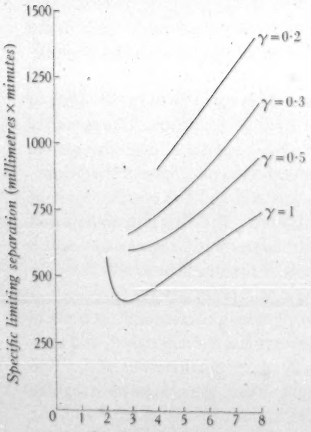

Figure 8. Brightness of the object, $0{\cdot}4 \times 10^{-8}$ candles/cm²

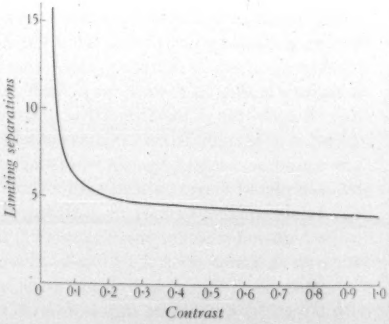

Figure 9.

This assemblage of diagrams (of which only a small part is reproduced here) gives complete information on the quantities s and σ as functions of the three variables γ, B and ω. From them all the curves which result from varying one or other of the three independent variables, the two others remaining constant, can be obtained, if desired. For example, figure 9 refers to a constant brightness $B = 0{\cdot}01$ (good illumination) and a constant aperture $\omega = 0{\cdot}54$; it gives the values of the limiting separation s as a function of the contrast γ. It will be seen that the limit increases as the contrast diminishes.

§ 7. CAUSES OF THE LIMITED RESOLVING-POWER OF THE EYE

What is the cause of the enormous disparity between the properties of the eye and the predictions of the theory of diffraction? Two causes may be acting, (1) the aberrations of the optical system of the eye and (2) the imperfect resolving-power of the retina. A similar set of circumstances occurs in the photography of distant objects, where the resolving-power is limited by the aberrations of the objective and by the imperfections of the plate (grain, thickness of the sensitized layer, diffusion of light in this layer). In the photographic case, the two kinds of imperfection can be studied independently; this is more difficult in the case of vision, because of the impossibility of studying the receptive properties of the retina apart from the optical system. An ingenious method was suggested by Mr Le Grand;* I will speak of it, although it lies outside my subject, because it is an application of a celebrated experiment by Thomas Young.

A system of interference fringes is produced on the retina by placing two parallel slits in front of the eye, and looking at a bright line. The aberrations of the optical system do not affect these fringes; their spacing can be altered by varying the distance between the slits, and the angular distance between consecutive fringes is in each case known. Again, the contrast can be varied by cutting down the light on one of the slits by means of a rotating sector; and the brightness is varied by altering the source of light. We have thus on the retina an exactly known test object; we can observe the disappearance of the fringes, due solely to the properties of the retina, as the slits are gradually separated, which gives the limit of separation of the retina alone. On the other hand, comparison with vision when the optical system takes part can be obtained by examining a set of interference fringes with no diaphragm over the eye, for example fringes from a Babinet's compensator, the spacing being easily varied by altering the distance of vision, and the contrast by variation of the polarizers.

I shall not speak of the results, since I wish to base my arguments on the facts of vision observed directly, and on their applications to optical instruments.

* *C.R. Acad. Sci.*, Paris, **200**, 490 (1935).

§ 8. APPLICATION TO A PERFECT OPTICAL INSTRUMENT

I assume that the instrument examined is *perfect*, i.e. that it gives images exactly in accordance with the theory of diffraction, that its transmission coefficient is 100 per cent, and that it gives no stray light.

The theory of diffraction asserts that the instrument separates a certain angular distance between two points or lines; it is by no means certain, or even probable, that we shall see the two points or lines as separated.

We have to consider the object space and the image space. What we see has reference to the object space: I see a man on yonder mountain, an aeroplane in the sky, and so on; but the properties of the eye refer to the image space. The relations between the two are given by geometrical optics, and the diffraction system follows the same laws: we may think of the diffraction system in the object space, and the perfect instrument gives the geometrical image of this system in the image space. Finally, the image of a point is a small disk (if we neglect the diffraction rings, which are very faint) in a microscope, just as in a telescope. This disk behaves like a true object, and follows the laws of geometrical optics; the eye looks through an aperture which, usually, is the exit pupil of the instrument. Exceptionally, as in the Galilean telescope and many periscopes, it is the opening of the pupil of the eye itself.

O Let us consider the case of a telescope. We have to consider the following quantities: Total diameter of the objective, O; effective diameter of the objective, Ω, I, ω_0 Ω; exit pupil, I; total diameter of the pupil of the eye, ω_0; effective diameter of the ω, M pupil of the eye, ω; magnification, M.

The laws of geometrical optics give

$$M = O/I \qquad \ldots\ldots(1).$$

Under the prevailing conditions of brightness (which are not altered by a perfect instrument) the eye with the effective pupil ω has a limit of separation s which is given by the above experiments. Transformed to the object space this limit be- S comes S, and it is this quantity which concerns us in judging the properties of the system formed by the instrument and the eye together. We have

$$S = s/M \qquad \ldots\ldots(2).$$

We must distinguish the case in which the exit pupil is smaller than the pupil of the eye from that in which it is larger; the value of ω which must be taken for calculating s is different in the two cases.

Case 1. Exit pupil of the instrument smaller than the pupil of the eye, $I < \omega_0$. This is the more common case. Then the pupil actually used is that of the instrument ($\omega = I$) and the whole of the objective is utilized ($\Omega = O$). Equations (1) and (2) then give

$$s\omega = S\Omega \qquad \ldots\ldots(3).$$

The left-hand side is the specific limit of the eye under the given conditions; the right-hand side $S\Omega$ or SO may be called the specific limit of separation of the σ, Σ combination, instrument and eye; these quantities being called σ and Σ, we have

$$\sigma = \Sigma.$$

The perfect instrument is that which does not spoil the specific properties of the eye.

Case 2. $I > \omega_0$.

Here the pupil of the eye is fully utilized and $\omega = \omega_0$. The preceding relations give

$$\Sigma = \sigma I/\omega_0.$$

If the magnification is changed, then I is altered without any variation of the pupil ω_0 or σ; as long as the relation $I > \omega_0$ remains true, the curve giving Σ as a function of I is a straight line passing through the origin.

Similar considerations apply to the microscope, but here we practically always have the first case.

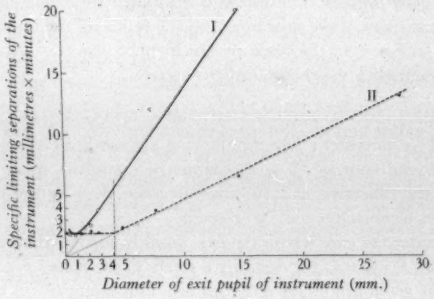

Figure 10. Curves showing the specific limiting separation for perfect instruments, as a function of the exit pupil. Normal eye, full curve; perfect eye, dotted curve. The diameter of the pupil of the eye is constant and equal to 4·05 mm.

Experimental verification. The preceding results have been verified by Mr Arnulf by means of a small telescope with a very good objective of diameter $O = 30$ mm. and a focal length $f = 285$ mm., by Hilger; a number of eyepieces giving magnifications from 1 to more than 1000 were used; for the lowest magnifications the eyepiece was another lens similar to the objective; then oculars of the usual types, and finally, for the highest powers, a microscope objective was used as eyepiece. In order to avoid possible variations in the diameter of the pupil of the eye, a circular diaphragm 4 mm. in diameter was always used. As test object, parallel lines with complete contrast ($\gamma = 1$) and high brightness were used. In each case the limit of separation was determined, and from it the specific limit Σ of the combination of the eye and instrument was deduced. The results are represented in a diagram in which the abscissae are the diameters of the exit pupil of the telescope (a quantity which varies as $1/M$, where M is the magnification) and the ordinates are the specific limits of separation. The theoretical curve consists of two parts: a linear part passing through the origin for all values of I greater than 4 mm., and a curved part for cases in which $I < 4$ mm. In the latter part we should have $\Sigma = \sigma$, and the curve is the same as that deduced from naked-eye observations (figure 3). In figure 10,

the full-line curve is the theoretical one; the observed values are shown by small circles. The agreement is very satisfactory.

If the eye were an instrument perfect in all respects and limited solely by diffraction we should still find two parts, but different from those given by the real eye. Curve II of the same figure (in dotted lines) represents the theoretical curve for this case; the part corresponding to $I < 4$ mm. gives a constant ordinate. To verify this conclusion, Mr Arnulf has constructed a model of a perfect eye as follows. At the end of the telescope studied, with its 4-mm. pupil in position, he placed a good objective of focal length 1 m. which, stopped down by the artificial pupil of diameter 4 mm., may be considered as perfect. The real image from this objective is projected on a ground glass, which acts as the retina. The effect of grain is eliminated by moving the glass rapidly. The image is examined by means of a magnifying-glass. Owing to the size of the final image on the retina all the imperfections of the eye disappear. In figure 10 the black points give the observed values; they are in excellent agreement with the theoretical curve.

§ 9. OPTIMUM CONDITIONS FOR OBTAINING A GIVEN EFFECT

It is desired to construct a telescope having a given limit of separation S for a given brightness and contrast. Two fundamental quantities must be chosen, the diameter O of the objective and the magnification M. Naturally, the smallest possible diameter of objective will be selected.

We will consider the case where the exit pupil is smaller than the pupil of the eye ($I < \omega_0$). Then $S \times O = \sigma$; the quantity σ refers to the naked eye for the pupil ω equal to I and the given brightness and contrast. This quantity σ is known from the above-mentioned curves as a function of I. Usually the curve giving σ as a function of ω has a minimum; this minimum corresponds to the most advantageous design. It determines the value of the exit pupil of the instrument as well as that of σ. The diameter of the objective is determined by equation (3), which gives $O = \sigma/S$, and, the exit pupil being known, we have the magnification $M = O/\omega$.

For high and medium brightness (e.g. between 1·5 and 0·10 stilb) the minimum of the specific limit of separation σ occurs for effective values of the exit pupil lying between 0·5 and 0·8 mm., whatever the contrast; we may reasonably take 0·7 mm. This leads to a magnification of 100 for an objective of diameter 70 mm. This is in accordance with the practice of astronomy for the observation of really bright surfaces like the moon and the major planets. Similar considerations apply to the microscope, for which exit pupils of the same order as those in practice are found. In the telescope, the objective diameter can be calculated from the limit of separation for a given contrast.

For the lower brightnesses, from 10^{-3} to 10^{-5}, the minimum of σ moves progressively towards large pupils, and the more so the smaller the value of B. For a fairly good contrast, say for $\gamma = 0{\cdot}3$, the optimum occurs for an exit pupil between 1 and 2 mm., which may rise to 4 mm. for the faintest contrasts.

Finally, for the lowest brightness, less than 10^{-8}, there is an advantage in taking the exit pupil as large as the pupil of the eye.

§ 10. TELESCOPES FOR TERRESTRIAL OBSERVATION AT NIGHT

The most characteristic case of observation at low brightness is that where objects are seen on a moonless night, with no other illumination than that from the sky. The brightness of the sky is of the order of 10^{-8} stilb, and that of objects on the ground is still less. It is well known that under these conditions visibility is very bad; only objects of great apparent diameter are seen. Let us consider for example a brightness of $0{\cdot}4 \times 10^{-8}$ and a test object of perfect contrast. Binoculars of the usual type may have for example a magnification of 8, with an objective of 32 mm. The preceding formulae lead to $14'$ as the limit of separation; vision is much worse than naked-eye vision in daylight.

If we could use much larger instruments without being stopped by consideration of weight, inconvenience and price, we could considerably improve vision at night. Take the same test object and consider how a telescope should be constructed to give at this feeble brightness the same limit of separation as the naked eye in full daylight, i.e. a limit of $1'$. We find that this result is attained with a 26-cm. objective and a magnification of 86. This is a large instrument whose employment would generally be impossible. And again, the brightness adopted is not the least which might be encountered. For $B = 1{\cdot}3 \times 10^{-10}$, it is found that the same result would be reached with a 250-cm. (100-in.) objective and a magnification of 250.

For strong brightnesses (daylight vision) the necessity for large pupils and large instruments is again found when the contrast is only slight. Take for example $B = 0{\cdot}15$ stilb (which is a very good brightness for objects in sunlight) but a very feeble contrast, $\gamma = 0{\cdot}02$. We wish to attain a limit of separation of $5''$. This is found to require a 92-mm. objective and a magnification of 21.

§ 11. IMPERFECT INSTRUMENTS

Let us take certain defined conditions of brightness and contrast and consider the specific limits of separation. A perfect instrument would give a limit Σ equal to the limit σ for the naked eye under the same conditions and for the same pupil-aperture; we have therefore $\Sigma = \sigma$. Now examine an imperfect instrument, and we find that it has a larger limit Σ' and we set $\Sigma' = \sigma'$ for the eye. The ratio $E = \sigma/\sigma'$ is called by Mr Arnulf the efficiency of the instrument; this definition allows the properties of entirely different instruments, such as a microscope and a telescope, to be compared with each other; nevertheless, it must be remarked that this efficiency depends greatly on the brightness and the contrast of the test object employed. Experiment shows that for test objects with complete contrast ($\gamma = 1$) and great brightness, as those of Foucault usually are, the efficiency nearly always has a value near 1, i.e. nearly all instruments appear to be almost perfect. This is not so if the brightness and contrast are lowered; measurement of the efficiency then permits the classification of instruments.

The imperfections of an instrument, which are marked by a decrease in E, can arise from two causes—(1) aberrations of all kinds, and (2) the presence of stray light. The latter effect is shown particularly at low values of the contrast. Suppose that a test object which has a background of uniform brightness B on which lines with a contrast γ are superposed is being examined. Stray light has the effect of
K adding a brightness KB over the whole field, where K is a stray-light coefficient. This has the effect of lessening the contrast of the marks, giving it the value

$$\gamma' = \gamma/(1+K).$$

This decrease in contrast has the effect of increasing the limit of separation, and the change is large if the contrast γ is already slight. The following table refers to a brightness B equal to 0·01 and a pupil ω equal to 0·54 mm.; it gives the values s of the limit of separation for different values of the contrast of the test object, for the values $K=0$ (absence of fogging) and $K=1$ (brightness of the stray light equal to that of the background).

Table

γ	s	
	$K=0$	$K=1$
1	3·9′	4·4′
0·1	6·1′	10′
0·05	10′	∞

The influence of stray light is slight when $\gamma=1$; it becomes rather large when $\gamma=0{\cdot}1$, and when $\gamma=0{\cdot}05$ fogging causes the complete disappearance of the test object.

This partly explains the difference between a laboratory test of an instrument and the use of the same instrument in the open air. In the former case a test object with great contrast is generally used on a dark background, which almost completely removes the effect of stray light; in the open air there are many objects with slight contrast, and stray light is of importance.

§ 12. RESULTS OF AN EXPERIMENTAL STUDY OF EFFICIENCY

The Adam Hilger objective previously mentioned was first studied. The diameter was 31 mm., the focal length 285 mm. and the aperture $f/9$. The objective was examined with various values of γ, with a well illuminated test object. Curve I of figure 11 gives the value of the efficiency. It will be seen that the efficiency is nearly always equal to 1, except at very slight contrasts where a slight fall is shown. The same objective, reversed, was then tested, so that a longitudinal spherical aberration of 3 mm. was introduced. Curve III gives the results obtained. Curve II refers to a simple non-achromatic lens, under the conditions in which it gave the best definition. It will be seen that when $\gamma=1$ the efficiency of the very bad instruments is sensibly equal to that of the perfect objective. But as the contrast diminishes, the differences in properties are brought out strongly.

Curve IV concerns the same simple lens, but with observations at the *circle of least confusion*. Under these conditions the images are very poor, and the low efficiency is shown even for a contrast of unity.

It may be concluded that laboratory examination of optical instruments could give information useful in practice if test objects with variable contrast were used.

It would also be of importance to examine the effect of stray light systematically. This light can occur in several ways. It can emanate from the actual object under examination, by scattering at the surfaces and in the material of the optical parts. It

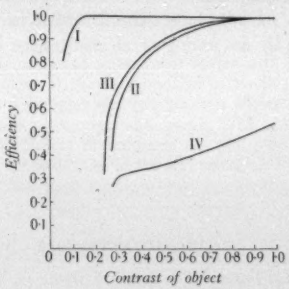

Figure 11. Variation of efficiency with contrast. I, excellent Hilger objective, $f=285$ mm., $O=31{\cdot}2$ mm.; II, simple plano-convex lens of same properties, at minimum of aberration; III, objective 1 reversed, spherical aberration approximately 3 mm., set at marginal extremity of axial sheet of caustic; IV, as III, set at the common point of the two sheets of the caustic.

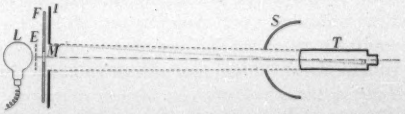

Figure 12. *L*, opal lamp illuminating test object; *E*, absorbing screen controlling brightness of test object; *M*, transparent test object; *F*, diffusing disk surrounding test object (lighted by lamps not shown); *I*, variable circular diaphragm, leaving exposed a diameter of the disk *F* corresponding to the field of the telescope *T*; *S*, diffusing sphere, whose illumination is not represented, supplying general light to illuminate instrument outside its field.

may also originate from light travelling in all directions, scattered in the instrument. Figure 12 shows the outline of an arrangement used by Mr Arnulf for the study of stray light. The test object, a transparency on glass, is illuminated by the opal glass lamp *L*, with the interposition if desired of a filter *E* to reduce the brightness. The test object is surrounded by the diffuser *F*, illuminated by lamps (not shown), and limited by an adjustable diaphragm *I*. We have thus the equivalent of an object of greater or less brightness, surrounded by a background whose brightness and area can also be varied. Finally, the diffusing sphere *S*, illuminated by lamps (not shown), gives the equivalent of the general light which is found in the open air.

§ 13. CONCLUSION

The preceding considerations will, I hope, have shown the importance of the properties of the eye in deciding what it is possible to *see* in an optical instrument. The practical constructor of optical instruments is forced to take many other factors into account, in particular weight, convenience of handling, conditions of use, and price; further, it is impossible for him to build a different instrument for each particular case. Certain cases, such as that of night observation, may derive benefit from the considerations set out above. On the other hand, users of instruments may make use of them by not asking of an instrument services which it cannot render.

535·338.4:546.17

THE PHENOMENON OF SPREADING IN THE FIRST POSITIVE BANDS OF NITROGEN

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Communicated by Prof. A. M. Tyndall, F.R.S., March 20, 1936.
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ABSTRACT. The paper describes an experiment designed to distinguish between two theories of secondary excitation of the first positive bands in nitrogen. The resonance radiation of nitrogen emitted from an electron beam is allowed to pass through a thin celluloid window which holds back metastable atoms. The results show that part, and possibly the whole, of the secondary excitation of the first positive bands is due to collisions of the second kind with molecules in the $a^1\Pi$ state.

§ 1. INTRODUCTION

It is well known that if an electron beam is projected into a gas at low pressure the light emitted is in general not confined to the beam. Some of the spectral lines are emitted at distances so far from its edges that they cannot possibly have been excited by direct electron-impact. Another group of lines, on the other hand, is emitted only from gas molecules actually within the beam, and for these we may assume that excitation is direct. The first group of lines we may call the *spreading lines*, the second the *non-spreading lines*. Spreading has been observed in mercury[1], in helium[2] and in nitrogen[3]. This paper describes an investigation of the mechanism of spreading for the first positive bands of nitrogen.

The secondary excitation process responsible for the production of spreading has been explained in two different ways by Maxwell[1] and by Skinner and Lees[2] respectively, and it is perhaps worth while to give here a brief summary of the essential points in the two theories.

Both theories agree that the spreading of resonance lines and of lines whose upper level is an upper level of a resonance line is due to absorption in the gas of resonance radiation produced by direct excitation in the electron beam. In helium, for example, this absorption produces atoms excited to ^1P states in the gas outside the beam, and these atoms can reradiate either the original resonance line or any line whose upper level is ^1P. This explanation agrees with the experimental observations. All lines starting from ^1P levels show strong spreading.

But there exist also lines which show strong spreading and whose upper levels cannot possibly be excited by optical absorption. Maxwell explains this by assuming that metastable atoms produced in the electron beam (either by direct excitation or by cascade) diffuse outwards into the body of the gas. They can here absorb

radiation from the beam, be raised in this way to a still higher level and so radiate the other spreading lines.

The grave difficulties in the way of Maxwell's explanation have been exhaustively discussed in the case of helium by Skinner and Lees[2] who propose an alternative explanation for the occurrence of the anomalous lines. They suggest that in these cases the spread light arises from collisions of the second kind between atoms in the ground state and atoms which have been raised to resonance levels outside the electron beam. Through these collisions atoms can be transferred to energy levels they could not reach by optical absorption; and so lines can spread which are not resonance lines. The Skinner-Lees theory is entirely consistent with the numerous experimental facts; but there was no absolute proof that it was correct.

The only way to distinguish certainly between the two theories was to arrange some experiment in which the whole light from the beam was allowed to pass into the surrounding gas and at the same time the diffusion of metastable ions was prevented. In the experiments to be described, the resonance radiation of nitrogen was allowed to pass through windows of extremely thin celluloid which partially transmitted radiation of all wave-lengths, at the same time holding back metastable atoms. Maurer and Wolf[4] have previously used a somewhat different method of eliminating metastable atoms and have rendered it practically certain that the explanation of Skinner and Lees is correct in the case of helium. Nevertheless it seemed worth while to carry out the investigation by a different method in the case of nitrogen, which shows certain peculiarities and for which a different mechanism might be at work. The resonance radiation of nitrogen extends from 1450 to below 1200 A. Fluorite completely absorbs the short-wave-length end of this spectrum, and where it transmits has a rapidly varying absorption coefficient. Celluloid had to be employed to make sure of getting the whole wave-length range.

§ 2. APPARATUS

Attempts to use low-pressure arcs in nitrogen as sources of resonance radiation were unsuccessful. For technical reasons it proved impossible to bring the main body of the discharge within a distance less than 4 cm. from the aperture of the resonance chamber without at the same time introducing electrons from the discharge. As the arcs would not run steadily at a pressure of less than 5×10^{-3} mm. of mercury the long column of gas must have absorbed strongly. No effects were observed, and the method was abandoned.

The experimental tube. We therefore returned to the original tube described in the paper of Thompson and Williams[3]. The experimental arrangements were essentially as described there except that the Faraday collector took various forms as the work progressed. The tube is shown diagrammatically in figure 1. The electrons are accelerated from the equipotential cathode K to the first slit S by a voltage V_1, about 115 volts. They then pass in succession through the focusing slit F whose potential V_2 can be varied to give the sharpest beam and through the

defining slit C whose voltage V_3 gives the final energy of the electrons in the beam. The Faraday box X collects the electrons and the milliammeter MA measures the current in the beam.

The Faraday cage first used was of the form shown in figure 1. The beam, the axis of which is shown dotted, thus passed parallel to the upper surface of X within a distance of 1 or 2 mm. With this arrangement it was found possible to produce a distinct tuft of spread light above the small aperture A cut in this surface. The pressures of nitrogen in the tube varied between 3 and 4×10^{-3} mm., and the beam currents between 2 and 3 mA.

Some preliminary attempts to observe spreading through a thin celluloid film, with a collecting-electrode essentially similar to that shown in the figure, were unsuccessful owing to the films breaking under the action of the discharge.

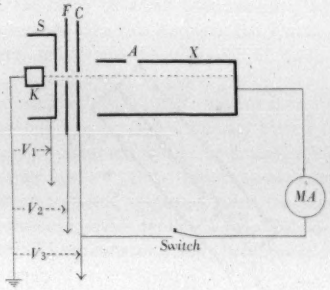

Figure 1.

The windows, which were of the order of 10^{-6} cm. thick, were prepared as described by O'Bryan[5]. A dilute solution of celluloid in amyl acetate was allowed to spread over a clean surface of distilled water, and after the solvent had evaporated a metal frame which was to carry the window was dropped on the film which adhered to it. The frame was then picked off and allowed to dry.

The windows so prepared usually appeared perfectly transparent. They were just visible by reflected light when held over a black background, and often presented a flawless surface when so examined. But some of them showed very faint silvery streaks covering perhaps a tenth of the total surface. These were perhaps due to traces of grease on the surface of the water; in any case they tended to disappear as the technique of cleanliness improved. It is worth pointing out, nevertheless, that some of the early, apparently imperfect windows turned out to be far more durable than the cleaner windows afterwards produced.

Although this form of collector proved ultimately unsuitable, the experience gained with it, and with other preliminary types, was useful in finding the best conditions under which spreading occurred. Moreover these early investigations showed that the rupture of the celluloid was not due to mechanical shock when the

apparatus was pumped out, that the windows could be stored *in vacuo* for periods of days, and that heating by radiation from the rather large hot cathode did not injure them. On the other hand a quite small current (10^{-4} A.) in the electron beam destroyed them in a few minutes, even though they were protected from the direct beam by a barrier. Thus there remained the possibility either that the windows had been charged up by the capture of electrons and were torn by electrostatic forces at their edges, or (what is more probable) that the slow electrons produced some chemical disintegration when they struck the film.

It was therefore necessary to design a collecting-box and resonance chamber in which the windows could be protected during the preliminary manipulation of the electron beam, and only exposed while an observation was actually being made.

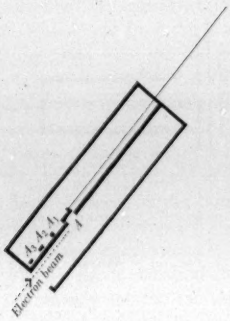

Figure 2.

Final form of the apparatus. The final form which the electrode took is shown diagrammatically in figure 2. A stainless-steel box was divided longitudinally by a metal septum. In this septum was a single circular aperture A, $2\frac{1}{2}$ mm. in diameter. The sides of the box were closed with thin glass windows carefully cleaned. Thus it was impossible for metastable atoms to diffuse into the resonance chamber without first striking a metal surface unless they passed through the aperture in the septum. This aperture could be closed by a rectangular metal slide moving in a longitudinal depression cut in the septum. The axis of the tube was tilted at an angle of 45° to the horizontal, so that the slide rested in equilibrium at the lowest point of the resonance chamber and closely in contact with the septum. This slide carried the celluloid windows. When it was in the extreme position as shown in the figure it closed the aperture. By means of a thin copper wire it could be drawn up so as to register the three holes A_1, A_2, A_3 in succession with the aperture in the septum. This operation could be performed when the electrode was inside the tube by means of a windlass and a greased joint. A circular scale on the windlass made it possible to say which window was in registration with A. Thus the preliminary

adjustments of the electron beam could be made while the celluloid windows on the slide were effectively screened from any direct action of the discharge. A switch was provided in the circuit from this electrode assemblage, figure 1, so that the electron beam could be quickly interrupted when necessary.

The apertures A_2 and A_3 were covered with a fine wire gauze made from No. 47 Eureka wire spot-welded into place. This had two purposes. First, it made the very thin windows afterwards used very much stronger mechanically. Secondly, it was hoped that the gauze would assist in conducting away any electrostatic charge which might be built up on the celluloid. The gauze had a mesh of $\frac{1}{2}$ mm. It was made by sandwiching a grid of Eureka wire between two copper flats and passing a gradually increasing current from a welding transformer through the assemblage. Alcohol was used as a flux. In this way the crossed wires were welded together at their intersections, and the gauze remained smooth.

The greatest care was taken to avoid contaminating either the slide or the Faraday collector with grease. On this account, the Faraday collector was never touched with the fingers except during a periodical readjustment of the whole electrode system. The slide was heated to about 300° C. in air before being covered with the celluloid windows, and after this treatment it was allowed to come into contact only with clean filter paper and previously heated forceps. Unless these precautions were rigorously observed, traces of grease would subsequently make their way on to the inner surface of the collecting-electrode and there become charged up by collecting scattered electrons from the beam. Local retarding-potentials were thus produced which rendered the electron beam diffuse and inhomogeneous in velocity. The grease could only be removed by long bombardment with heavy electron current.

The apertures were covered by celluloid windows in the manner already described, the slide was hooked to the copper wire and manipulated into its groove. The electrode assemblage, which was carried on a ground joint, was then returned to the tube.

§ 3. OBSERVATIONS

The routine of observation was as follows. The tube was pumped down after the windows had been inserted, and the cathode was outgassed with no accelerating potentials on any of the slits. Nitrogen was now streamed through at a pressure of about 4×10^{-3} mm. and the intermediate slits were cleaned up by passing a heavy current (up to 200 mA.) to them from the filament. During the process the switch in the collector circuit was left open so that no electron beam passed through the Faraday collector. Even with the switch open there remained a faint luminosity due to a beam of positive ions as described by Thompson and Williams[3]. In the earlier stages of the discharge it had a greenish colour and presumably consisted of positive ions of mercury, an impurity which could otherwise be easily detected by using an electron beam too slow to excite the spectrum of nitrogen, and examining the light with a small spectroscope. The prominence of the mercury spectrum in the ion beam is presumably to be explained by a much higher efficiency of ioni-

zation for mercury than for nitrogen under the given discharge conditions. In any case this light became much fainter after the tube had run for half an hour, and negligible compared with the nitrogen light emitted by the direct electron beam. An appreciable amount of mercury vapour seemed to inhibit the spreading of the first positive bands, even though the mercury spectrum appeared very much fainter in total intensity than the nitrogen spectrum, and it was found worth while in consequence to admit air into the tube when necessary in such a way that mercury vapour could not be carried over from the liquid-air trap.

The beam was now allowed to pass into the Faraday box by closing the switch, and it was made as sharp as possible by altering the position of the cathode or the potential of the focusing-slit. The energy of the electrons in the beam was usually between 17 and 19 volts, and the current from 3 to 4 mA. The voltage was usually adjusted to give the best compromise between a good beam and intense spreading. In all the final experiments a low-voltage beam was employed in the manner described above. Some of the earlier experiments were carried out with a high-voltage beam, because larger currents can be readily obtained at, say, 50 volts than at 18 volts, yet the intensity per milliampere of the spread light is fainter. A more serious objection to the high-voltage beams was their great tendency to instability at high current-densities and high pressures. It seemed to be due to a form of very high-frequency oscillation such as has already been described in connexion with low-voltage arcs. In its limiting form it showed up as a sudden increase in the brightness of the beam, which, however, retained the characteristic purple colour of the negative bands (N_2^+) and of the second positive bands. Around it was a strong pinkish glow quite different in appearance from the ruddy spreading of the low-voltage beam, and containing not only the first positive but also the second positive bands. On the opening of the switch so that no resultant current could flow to the Faraday cage, the beam would frequently only alter slightly in appearance, although no current could flow through the milliammeter. There were, however, less pronounced forms of the same behaviour, characterized by abrupt alterations in the character of the beam as the accelerating potential was slowly altered. With the 18-volt beam, however, none of these phenomena were observed; there was a steady alteration in the brightness and shape of the beam as the voltage was altered, and (provided the collector box was free of grease) the excited light disappeared throughout a range of less than a quarter of a volt when the potential fell to the critical voltage.

As soon as conditions were satisfactory, all direct light from the filament and from the discharge was screened from the observer's eye; the beam was switched off, and the aperture A_1 was brought into registration with the hole in the septum. This aperture carried no gauze, and usually the celluloid film on it was deliberately demolished before it was put into the tube, although in fact it seldom resisted exposure to the side of the beam for more than half a second. The beam was then switched on, and the spreading into the resonance chamber was examined. It showed as a faint tuft of ruddy light escaping into the resonance chamber through the open aperture. If the spreading seemed strong enough the beam was switched

off, and the celluloid window A_2 was brought into registration with the hole. The beam was then switched rapidly on and off, the resonance chamber being meanwhile examined for spreading. The same observation was then made through A_3 and the results were noted down. The nitrogen stream was then stopped, air was let into the apparatus, and the condition of the windows on the slide was examined. Usually several panes of the celluloid were ruptured even with this brief exposure to the beam, but in one or two lucky cases the window remained more or less intact. Visual observation had to be employed because of the extremely short life of the windows under the given discharge conditions.

§ 4. RESULTS

The early series of experiments using windows 10^{-6} cm. in thickness showed no apparent spreading into the resonance chamber through the celluloid, even though one or two panes (about $\frac{1}{10}$ or more of the surface) were broken when the slide was examined afterwards. Rough estimates suggested that if the light in the resonance box had been as small as $\frac{1}{6}$ of the original intensity it would have been detectable. O'Bryan's absorption curves give a transmission of at least $\frac{1}{3}$ for the Lyman resonance radiation for windows 10^{-6} cm. thick. Since on the Skinner-Lees theory of spreading the intensity of the spreading should be proportional to that of the resonance radiation, these results seemed to be rather opposed to that theory. However, on one occasion a somewhat more dilute solution of celluloid, giving windows $0{\cdot}8 \times 10^{-6}$ cm. thick, was prepared. With a rather strong beam (5 mA.) a faint spreading into the resonance chamber through the window could be seen. Although the window was not quite intact on removal this provisional positive result gave encouragement for further investigation.

In all subsequent experiments windows only 5×10^{-7} cm. in thickness were used. Celluloid films of this tenuity are very fragile. They have also proved somewhat less resistant to the destructive action of the discharge than have the thicker windows. A large number of trials of the thin celluloid windows were made after experimental conditions had been made as good as possible. In only two experiments were windows removed intact, and in these cases faint spreading into the resonance chamber was definitely noticed. But the positive evidence for spreading through the celluloid does not rest only on these two observations. Several more observations of spreading, about 8 in all, were made through windows punctured only at one point, and with about 90 per cent of their surface unbroken. In these cases also spreading could be seen extending over the unbroken surface of the window. There is therefore good evidence to the effect that this form of spreading does take place through thin celluloid windows.

§ 5. DISCUSSION OF RESULTS

For the purposes of reference a diagram of the relevant energy levels of nitrogen is given, figure 3[6]. The band system with which we are concerned arises from the transition $B^3\Pi \rightarrow A^3\Sigma$, and most of the bands which contribute intensity to the visible radiation originate on levels below the twelfth vibrational level of the $^3\Pi$ state. The second positive bands, which do not show spreading, correspond to the transition $C^3\Pi \rightarrow B^3\Pi$. The only strong singlet system which can concern us is the Lyman-Birge-Hopfield system $a^1\Pi \rightarrow X^1\Sigma$; bands of this system whose lower level is the ground level of nitrogen form the resonance bands. The Vegard-Kaplan system $A^3\Sigma \rightarrow X^1\Sigma$ is the only known intercombination*; it is extremely weak and is excited only under special conditions. Thus the $A^3\Sigma$ level is for practical purposes metastable.

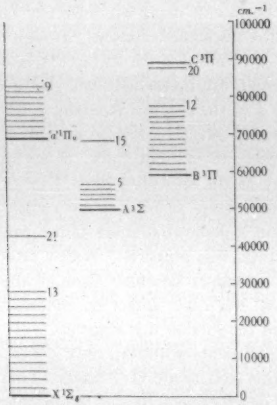

Figure 3. Energy levels of nitrogen.

Thus spreading could be explained *a priori* as due either to collisions of the second kind or to absorption by metastable molecules. Our experiment shows, however, that at least some part of the secondary light is due to the former process. There arises here the apparent difficulty that if such collisions are to occur before the molecule in the $^1\Pi$ state reradiates normally, then the effective cross section of the molecule in this state for a collision of this type must be some hundreds of times as great as the gas-kinetic cross section of the normal molecule. But these very large effective cross sections are not uncommon. It is known that if, during a collision of the second kind, most of the energy of excitation of the one molecule is transferred as excitation energy to the second molecule, so that little of the original

* This intercombination fixes the A level with respect to the ground state X.

energy goes into kinetic energy of translation, then the process may become extremely probable. This was predicted theoretically by Kallman and London[7] and verified experimentally by Duffendack[8] for atomic collisions. The latter reports effective cross sections which may be as much as 10^5 times larger than the gas-kinetic area. It is clear from figure 3 that a molecule in any of the vibrational levels of the $^1\Pi$ state can transfer its energy to excite lower states of the $B^3\Pi$ level. Moreover, owing to the very closely spaced vibrational-rotational levels of the ground state, the excess energy can remain as energy of vibration and rotation; and the condition for a large effective cross section is satisfied.

There remains the question whether the whole of the secondary light is to be explained by the mechanism suggested. It is of course impossible to make any definite statement on this point without a photometric comparison of the intensity of the secondary light with and without the interposition of the celluloid window. Although it has been pointed out in the discussion of the results that the intensity seemed to be reduced by the celluloid somewhat more than was to be expected on the basis of O'Bryan's absorption coefficients, nevertheless too much weight cannot be attached to this fact in view both of the difficulty of comparing visually the intensity of two light-sources near the threshold of visibility, and of the fact that the transmissibility of the films seemed to vary somewhat with their mode of preparation.

§ 6. ACKNOWLEDGMENT

I take the opportunity here of expressing my sincere thanks to Mr S. E. Williams who collaborated with me for a time during the earlier part of this work.

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548.7

AN IMPROVED NUMERICAL METHOD OF TWO-DIMENSIONAL FOURIER SYNTHESIS FOR CRYSTALS

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ABSTRACT. It is shown that a two-dimensional Fourier summation for a crystal without a centre of symmetry can be resolved into one-dimensional summations, and these latter can be calculated very rapidly by using a set of printed strips which give cosine and sine waves of different wave-lengths and amplitudes. The most useful interval of division of the strips, and various features concerning their use, are described.

§ 1. INTRODUCTION

A method has been described by J. M. Robertson[1] whereby the summation of a two-dimensional Fourier series is reduced to the processes of first arranging sets of figures, and of then adding them. The method described in the present paper is similar to this, but the process of arrangement is very greatly reduced, and since most of the time taken is concerned with the additions it is claimed that the method is as quick as any numerical method can possibly be.

The method is based on that described by the authors[2]. Essentially this reduces the computations to the addition of a number of one-dimensional cosine and sine terms. There are thus only two variables, the amplitude and wave-length of each cosine or sine wave, and the number of combinations of these to cover most cases is sufficiently small for it to be practicable to prepare them in advance. This has been done by the authors, the numbers representing the various waves being printed on cardboard strips. The present paper describes the derivation and use of such a set of strips.

§ 2. THEORETICAL CONSIDERATIONS

Division of the area of the projection. It has been shown[3] that if a radiation of
λ, θ wave-length λ be used, and if all reflections with glancing angles less than θ be observed, then Fourier synthesis will not show any detail finer than $0{\cdot}6\lambda/2 \sin\theta$. If $\lambda = 1{\cdot}54$ A. (for $K\alpha$ radiation of copper) and $\sin\theta = 1$, this quantity is $0{\cdot}46$ A. Thus it is necessary that the points at which the electron-density is computed should be appreciably closer together than this; but any undue closeness will be unnecessary as it will not reveal any greater detail.

Thus for most ordinary projections, the edges† of which are between 8 and 15 A.,

† These will not be the edges of the unit cell unless the crystallographic axes are orthogonal.

a division into about 50[4] parts would be suitable. This number, however, has some disadvantages. For instance points with co-ordinates $\frac{1}{4}$ are not included explicitly, and it is sometimes important that the electron-density at such points should be known accurately. This defect may be overcome by dividing the edge into 48[5] or 60[1] parts, and this also makes the work of preparation of the tables rather lighter. The latter number was chosen because it extends the limit of applicability of the method somewhat.

Adaptability to extreme cases. The division of the cell-edges into 60 parts is directly suitable if the maximum indices are each between 11 and 20. If one of the maximum index-values is below 11 (i.e. if one cell-dimension is small) it will be advisable to make the interval of division of the corresponding edge $\frac{1}{30}$. This may be done most simply by considering that we are going to perform a synthesis of two unit cells, the short edge being considered as doubled. One of the indices of each plane referred to this doubled cell will be doubled. Thus all we have to do in order to obtain an interval of $\frac{1}{30}$ in any direction is to double the corresponding indices of the Fs and proceed in the usual way. The strips will then give the projection over the range 0 to 0·50 directly, instead of from 0 to 0·25. Similarly, if the maximum index in one direction is 6, the indices corresponding to this direction may be trebled, and the interval of division will be $\frac{1}{20}$. The general rule is that the tables should be used as near as possible to their maximum index 20.

If, on the other hand, the maximum index exceeds 20 the strips as prepared by the authors will not be comprehensive. It will be desirable to make the interval of division $\frac{1}{120}$, in which case the indices must be halved. Thus the odd indices cannot be included, and their contribution will have to be computed by the ordinary method. Nevertheless, unless both ranges of index are greater than 20, it will be possible to use the strips directly in the final tables which involve the greater part of the work.

Expression of the general case in terms of one-dimensional series. The most general case (so long as the wave-length used is not near an absorption edge of any of the atoms concerned) is that of the completely asymmetric projection, in which the only relation between the Fs is $F(hk0) = F^*(\bar{h}\bar{k}0)$, where F^* is the conjugate complex of F. The direction of projection is taken as parallel to the c axis. F, F^*, $\bar{h}$,

If x and y are the co-ordinates of any point in the projection in fractions of 2π, and H and K are the maximum values of h and k in the array of Fs, the summation required is as follows, $F(hk)$ being now written for $F(hk0)$ x, y H, K

$$\sum_{-H}^{H}\sum_{K}^{K} F(hk)\exp i(hx+ky)$$

$$=\sum_{-H}^{H}\sum_{1}^{K}\{F(hk)\exp i(hx+ky)+F^*(hk)\exp -i(hx+ky)\}$$

$$+\sum_{1}^{H}\{F(h0)\exp ihx+F^*(h0)\exp -ihx\}$$

$$+F(00).$$

Since $F(hk)$ and $F(\bar{h}\bar{k})$ are conjugate, they may be expressed respectively as
δ $|F(hk)| \exp i\delta(hk)$ and $|F(hk)| \exp -i\delta(hk)$, and the expression becomes,

$$\sum_{-H}^{H}\sum_{1}^{K} |F(hk)| \{\exp i[hx+ky+\delta(hk)] + \exp -i[hx+ky+\delta(hk)]\}$$
$$\sum_{1}^{H} |F(h0)| \{\exp i[hx+\delta(h0)] + \exp -i[hx+\delta(h0)]\}$$
$$+F(00)$$
$$= 2\sum_{-H}^{H}\sum_{1}^{K} |F(hk)| \cos[hx+ky+\delta(hk)] + 2\sum_{1}^{H} |F(h0)| \cos[hx+\delta(h0)]$$
$$+F(00).$$

C Let $|F(hk)| \cos\delta(hk) = C(hk)$

S and $|F(hk)| \sin\delta(hk) = S(hk)$.

Then we have

$$2\sum_{-H}^{H}\sum_{1}^{K} \{C(hk)[\cos hx \cos ky - \sin hx \sin ky]$$
$$-S(hk)[\sin hx \cos ky + \cos hx \sin ky]\}$$
$$+2\sum_{1}^{H} \{C(h0)\cos hx - S(h0)\sin hx\}$$
$$+F(00)$$

which, for the purposes of summation is put into the form

$$2\sum_{1}^{H}\sum_{1}^{K} \{C(hk)[\cos hx \cos ky - \sin hx \sin ky]$$
$$-S(hk)[\sin hx \cos ky + \cos hx \sin ky]$$
$$+C(\bar{h}k)[\cos hx \cos ky + \sin hx \sin ky]$$
$$(\bar{h}-Sk)[-\sin hx \cos ky + \cos hx \sin ky]\}$$
$$+2\sum_{1}^{K} \{C(0k)\cos ky - S(0k)\sin ky\}$$
$$+2\sum_{1}^{H} \{C(h0)\cos hx - S(h0)\sin hx\}$$
$$+F(00)$$
$$= 2\sum_{1}^{H}\sum_{1}^{K} \{[C(hk)+C(\bar{h}k)]\cos hx \cos ky$$
$$-[C(hk)-C(\bar{h}k)]\sin hx \sin ky$$
$$-[S(hk)-S(\bar{h}k)]\sin hx \cos ky$$
$$-[S(hk)+S(\bar{h}k)]\cos hx \sin ky\}$$
$$+2\sum_{1}^{K} \{C(0k)\cos ky - S(0k)\sin ky\}$$
$$+2\sum_{1}^{H} \{C(h0)\cos hx - S(h0)\sin hx\}$$
$$+F(00).$$

The preliminary tables would then be concerned with the evaluation of

$$2\sum_{1}^{H}\{C(h\text{o})\cos hx - S(h\text{o})\sin hx\} + F(\text{oo}) = A(\text{o}, x), \text{ say,} \qquad A$$

of

$$2\sum_{1}^{H}\{[C(hk)+C(\bar{h}k)]\cos hx - [S(hk)-S(\bar{h}k)]\sin hx\} + 2C(\text{o}k) = A(k, x),$$

and of

$$2\sum_{1}^{H}\{[C(hk)-C(\bar{h}k)]\sin hx + [S(hk)+S(\bar{h}k)]\cos hx\} + 2S(\text{o}k) = B(k, x). \qquad B$$

$A(k, x)$ and $B(k, x)$ are evaluated separately for each value of k from 1 to K.

The final summation is then given by

$$A(\text{o}, x) + \sum_{1}^{K} A(k, x)\cos ky - \sum_{1}^{K} B(k, x)\sin ky.$$

Thus even the general expression can be reduced to the summation of one-dimensional series. In practice, however, this case is not important, as the values of $C(hk)$ and $S(hk)$ are not determinable by experiment. If, however, the projection has a centre of symmetry at the origin (which may be produced by a two-fold axis in the structure perpendicular to the plane of projection)

$$F(hk) = F(\bar{h}\bar{k})$$

and thus the Fs are real.

$$\therefore\ C(hk) = F(hk) \quad \text{and} \quad S(hk) = \text{o}.$$

In this case

$$A(\text{o}, x) = 2\sum_{1}^{H}\{F(h\text{o})\} + F(\text{oo}),$$

$$A(k, x) = 2\sum_{1}^{H}\{[F(hk)+F(\bar{h}k)]\cos hx\} + 2F(\text{o}k),$$

and

$$B(k, x) = 2\sum_{1}^{H}\{[F(hk)-F(\bar{h}k)]\sin hx\}.$$

The projection may have other symmetries which involve relationships between $F(hk)$ and $F(\bar{h}k)$. In such cases the summation is even simpler.

§ 3. PRACTICAL DETAILS

Derivation of numbers. The complete equipment as prepared by the authors consists of 2079 cosine strips and 1980 sine strips. The cosine strips have index-values o to 20 inclusive, and the sine strips 1 to 20 inclusive. For each index we have strips of amplitudes $\overline{99}$ to 99. The functions are plotted at intervals of 6° so that the strip corresponding to $A\sin hx$, for example, has printed on it the value of $A\sin(2\pi nh/60)$, correct to the nearest whole number, where n has values from o to 15. Each strip has the corresponding negative function on the back. As an example the sine strip for index 3 and amplitude 99 is:

99	S 3	0	31	58	80	94	99	94	80	58	31	0	$\overline{31}$	$\overline{58}$	$\overline{80}$	$\overline{94}$	$\overline{99}$

The strips are cut from a number of tables, each table having one index of cosine or sine with the amplitudes in successive rows.

The different tables are printed from the same columns of type merely arranged in different ways. For example, if the columns for sine 1 are numbered 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, then for sine 2 we have the arrangement of columns 0, 2, 4, 6, 8, 10, 12, 14, 14, 12, 10, 8, 6, 4, 2, 0; and for cosine 6 we have the order: 15, 9, 3, $\bar{3}$, $\bar{9}$, $\overline{15}$, $\bar{9}$, $\bar{3}$, 3, 9, 15, 9, 3, $\bar{3}$, $\bar{9}$, $\overline{15}$, the superior negative signs indicating that all the numbers in the column are negative instead of positive.

The area of summation. If we deal with crystals for which the projection possesses a centre of symmetry it is necessary to obtain the projection for only half of the unit cell. Sometimes the projection will have other symmetry elements which will still further reduce the area to be evaluated. The largest area which will have to be dealt with is given by the conditions that one parameter must go from 0 to 0·50 and the other from 0 to 1·00. This area can, however, easily be derived from the area 0 to 0·25 by 0 to 0·25 which is the area covered directly by the strips. The general rule which enables this extension of area to be effected is that in carrying out any of the one-dimensional summations even indices and odd indices must be kept separate. If, for example, we are summing cosine terms, we see that $\cos hx$ is symmetrical about $x=0{\cdot}25$ when h is even, and is antisymmetrical about $x=0{\cdot}25$ when h is odd. Thus, if in the summation we keep separate the terms with h even and h odd, we have only to add and subtract the two sets of totals in order to obtain the sums for $x=0$ to 0·25 and $x=0{\cdot}50$ to 0·25, respectively. In the case of sine terms we sum first for the planes with h odd, and then for those with h even. Sum and difference then give $x=0$ to 0·25 and $x=0{\cdot}50$ to 0·25, respectively. These ways of extending the range are illustrated in table 3, where they are applied to the summations of $\cos ky$ and $\sin ky$.

To extend the range of a parameter to 0·50 to 1·00 we notice that all the cosine terms are symmetrical about 0·50 whilst all the sine terms are antisymmetrical about this point. We therefore have to subtract sine terms from cosine terms to give the range 0 to 0·50 and to add them to give the range 1·00 to 0·50. In this way we derive the whole of the projection. The process is illustrated in table 4.

Storage of strips. The strips are kept in two similar wooden boxes [7], one for cosine strips and one for sines. All the strips of one index are kept in one compartment, the partitions between the compartments being made of aluminium. The sloping sides of the boxes ensure that on removal of one strip from a compartment its place shall be left open for its reinsertion. If desired the boxes may be made portable by fitting them with lids, some device being used to clamp the strips.

§ 4. PRECAUTIONS AGAINST ERRORS

Mistakes in the use of the strips can arise either from selection of the wrong strip or from errors in addition of the numbers. The former can be guarded against by a simple check. The strips are removed from the boxes by selecting the index, and then the amplitude required for that index, and so on, the order of consideration

being thus index, amplitude, index, amplitude, and so on. They should be checked by a glance down the index column, which will in general be 1, 3, 5, 7,... or 0, 2, 4, 6,..., and then by looking down the amplitude column, with special attention to signs. Mistakes in adding will be guarded against by the repetition of each addition. Especial care should be taken over the preliminary tables as an error here will run through a large part of the work.

If desired a complete check could be made by carrying out the summation the other way round. If for example the synthesis was done by first collecting the Fs with the same h in the preliminary tables and multiplying by the cos ky functions, it could be repeated by collecting first the Fs with the same k and multiplying by the cos hx functions. Usually, however, it will be enough to work out one line of the synthesis in this way.

§ 5. EXAMPLE OF THE USE OF THE STRIPS

In order to compare the procedure with that of the method previously described [2] the same example will be used.

Table 1 shows the values of $F(hk)$ for $CuSO_4.5H_2O$, which has only centrosymmetry. It will be observed that the maximum value of h is 8, whereas that of k is 13. It is therefore advisable to sum first with respect to k, so that the largest summations are confined to the shorter preliminary tables. Moreover, since the maximum value of h is only 8, the h indices may be multiplied by 2 in order to double the interval of division along the corresponding edge of the projection.

Table 1. Values of $F(hk0)$

$F(hk0) = F(\bar{h}\bar{k}0)$

k \ h	$\bar{8}$	$\bar{7}$	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	1	2	3	4	5	6	7	8
0	8	11	12	0	28	0	33	26	129	26	33	0	28	0	12	11	8
1		11	0	20	0	21	$\bar{18}$	30	0	18	10	19	$\bar{10}$	0	0	0	
2		0	0	0	0	$\bar{21}$	0	$\bar{17}$	12	$\bar{32}$	17	$\bar{7}$	10	0	9	0	
3		0	0	18	7	26	$\bar{20}$	23	11	50	17	18	7	16	6	8	
4		0	18	13	26	8	27	17	0	0	17	10	8	0	10		
5		0	0	0	0	12	0	0	$\bar{14}$	11	$\bar{15}$	0	$\bar{10}$	0	0		
6		0	0	0	7	0	16	0	12	14	15	0	9	0	0		
7		7	0	13	9	19	15	21	15	18	0	19	7	15			
8		0	10	0	0	0	16	$\bar{8}$	12	0	11	0	0	0			
9			0	0	0	0	$\bar{11}$	0	0	0	0	7	0				
10			8	0	12	0	14	7	16	0	10	0	12				
11				13	0	12	0	17	0	8	0	7					
12				0	0	0	0	0	0	0	0						
13					0	0	0	11	0	7							

It is convenient next to prepare tables 2*a* and 2*b* which give the values of $F(hk)+F(\bar{h}k)$ and $F(hk)-F(\bar{h}k)$ respectively. Where one index is zero the values of $F(h0)$ and $F(0k)$ only are used, and the value of $F(00)$ is divided by 2. Comparison with the general formula will show that this is equivalent to dividing the whole series by 2, the smaller numbers making the subsequent additions less laborious. This process will be different in cases of higher symmetry for which, for example $F(hk)=F(\bar{h}k)$, when the series may be divided by 4. Then the numbers in table 2*b* will be zero, and in table 2*a* will be the single F values, except that $F(h0)$ and $F(0k)$ will be divided by 2, and $F(00)$ by 4. The process is most easily visualized in terms of the reciprocal lattice[6]. To each point (h, k) of the *ab* section of the lattice is attached a weight $F(hk)$. If $F(hk)=F(\bar{h}k)$ each weight $F(hk)$ occurs four times, $F(0k)$ and $F(h0)$ twice, and $F(00)$ once.

Table 2*a*

Values of $F(hk0)+F(\bar{h}k0)$.

		2*h*								
		0	2	4	6	8	10	12	14	16
	0	65	26	33	*0*	28	0	12	11	8
	2	12	$\overline{49}$	17	$\overline{28}$	10	0	9	0	
	4	0	17	44	*18*	34	13	28	0	
k	6	12	14	31	*0*	16	0	0	0	
	8	12	$\overline{8}$	27	*0*	0	0	10	0	
	10	16	7	24	*0*	24	0	8		
	12	0	0	0	*0*	0	0			
	1	0	48	$\overline{8}$	*40*	$\overline{10}$	20	0	11	
	3	11	73	$\overline{3}$	*44*	14	34	6	8	
	5	$\overline{14}$	11	$\overline{15}$	*12*	$\overline{10}$	0	0	0	
k	7	15	39	15	*38*	16	28	0	7	
	9	0	0	$\overline{11}$	*7*	0	0	0		
	11	0	25	0	*19*	0	13			
	13	0	18	0	*0*	0				

Table 2*b*

Values of $F(hk0)-F(\bar{h}k0)$

		2*h*								
		0	2	4	6	8	10	12	14	16
	0	0	0	0	*0*	0	0	0	0	0
	2	0	$\overline{15}$	17	*14*	10	0	9	0	
	4	0	$\overline{17}$	$\overline{10}$	*2*	$\overline{18}$	$\overline{13}$	$\overline{8}$	0	
k	6	0	14	$\overline{1}$	*0*	2	0	0	0	
	8	0	8	$\overline{5}$	*0*	0	0	$\overline{10}$	0	
	10	0	$\overline{7}$	$\overline{4}$	*0*	0	0	$\overline{8}$		
	12	0	0	0	*0*	0	0			
	1	0	$\overline{12}$	28	$\overline{2}$	$\overline{10}$	$\overline{20}$	0	$\overline{11}$	
	3	0	27	37	$\overline{8}$	0	$\overline{2}$	6	8	
	5	0	11	$\overline{15}$	$\overline{12}$	$\overline{10}$	0	0	0	
k	7	0	$\overline{3}$	$\overline{15}$	*0*	$\overline{2}$	2	0	$\overline{7}$	
	9	0	0	11	*7*	0	0	0		
	11	0	$\overline{9}$	0	$\overline{5}$	0	$\overline{13}$			
	13	0	4	0	*0*	0				

Tables 3*a* and 3*b* are the parts of the preliminary tables for which $2h=6$, and in these tables the actual strips used are depicted. Of course, only the totals would be written down. The amplitude columns of the strips used in tables 3 correspond with columns (shown in italics) in table 2*a* and 2*b*. The results of tables 3*a*, 3*b* are given in the rows designated "difference" and "sum", which give the totals corresponding to the two ranges of y, 0 to 15/60, and 30/60 to 15/60.

The results of all the preliminary tables for the different values of h are collected in a table 3*c*, not shown. This table then serves for the construction of the final tables, of which table 4 shows the portion for $y=7/60$. Each set of strips has its amplitude column taken from table 3*c*, and the difference and sum of the cosine and sine parts gives a line of the final totals.

Table 3*a*

Evaluation of $\frac{1}{2}A(2h, y)$ for $2h = 6, = \sum_{1}^{K}[F(6k) + F(\bar{6}k)] \cos ky + F(6o)$

	y (60ths)															
	0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*
$\overline{28}$ *C* 2	$\overline{28}$	$\overline{27}$	$\overline{26}$	$\overline{23}$	$\overline{19}$	$\overline{14}$	$\overline{9}$	$\overline{5}$	3	9	14	19	23	26	27	28
18 *C* 4	18	16	12	6	$\overline{2}$	$\overline{9}$	$\overline{15}$	$\overline{18}$	$\overline{18}$	$\overline{15}$	$\overline{9}$	$\overline{2}$	6	12	16	18
	$\overline{10}$	$\overline{11}$	$\overline{14}$	$\overline{17}$	$\overline{21}$	$\overline{23}$	$\overline{24}$	$\overline{21}$	$\overline{15}$	$\bar{6}$	5	17	29	38	43	46
40 *C* 1	40	40	39	38	37	35	32	30	27	24	20	16	12	8	4	0
44 *C* 3	44	42	36	26	14	0	$\overline{14}$	$\overline{26}$	$\overline{36}$	$\overline{42}$	$\overline{44}$	$\overline{42}$	$\overline{36}$	$\overline{26}$	$\overline{14}$	0
12 *C* 5	12	10	6	0	$\bar{6}$	$\overline{10}$	$\overline{12}$	$\overline{10}$	$\bar{6}$	0	6	10	12	10	6	0
38 *C* 7	38	28	4	$\overline{22}$	$\overline{37}$	$\overline{33}$	$\overline{12}$	15	35	36	19	$\bar{8}$	$\overline{31}$	$\overline{38}$	$\overline{25}$	0
7 *C* 9	7	4	$\bar{2}$	$\bar{7}$	$\bar{6}$	0	6	7	2	$\bar{4}$	$\bar{7}$	$\bar{4}$	2	7	6	0
19 *C* 11	19	8	$\overline{13}$	$\overline{18}$	$\bar{2}$	16	15	$\bar{4}$	$\overline{19}$	$\overline{11}$	9	19	6	$\overline{14}$	$\overline{17}$	0
	160	132	70	17	0	8	15	12	3	3	3	$\bar{9}$	$\overline{35}$	$\overline{53}$	$\overline{40}$	0
Difference	150	121	56	0	$\overline{21}$	$\overline{15}$	$\bar{9}$	$\bar{9}$	$\overline{12}$	$\bar{3}$	8	8	$\bar{6}$	$\overline{15}$	3	46
Sum	$\overline{170}$	$\overline{143}$	$\overline{84}$	$\overline{34}$	$\overline{21}$	$\overline{31}$	$\overline{39}$	$\overline{33}$	$\overline{18}$	$\bar{9}$	2	26	64	91	83	
	30	*29*	*28*	*27*	*26*	*25*	*24*	*23*	*22*	*21*	*20*	*19*	*18*	*17*	*16*	*15*
	y (60ths)															

Table 3*b*

Evaluation of $\frac{1}{2}B(2h, y)$ for $2h = 6, = \sum_{1}^{K}[F(6k) - F(\bar{6}k)] \sin ky$.

	y (60ths)															
	0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*
$\bar{5}$ *S* 1	0	0	0	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{5}$	$\bar{5}$	$\bar{5}$	$\bar{5}$	$\bar{5}$	$\bar{5}$	$\bar{5}$
8 *S* 3	0	$\bar{2}$	$\bar{5}$	$\bar{6}$	$\bar{8}$	$\bar{8}$	$\bar{8}$	$\bar{6}$	$\bar{5}$	$\bar{2}$	0	2	5	6	8	8
$\overline{12}$ *S* 5	0	$\bar{6}$	$\overline{10}$	$\overline{12}$	$\overline{10}$	$\bar{6}$	0	6	10	12	10	6	0	$\bar{6}$	$\overline{10}$	$\overline{12}$
7 *S* 9	0	6	7	2	$\bar{4}$	$\bar{7}$	$\bar{4}$	2	7	6	0	$\bar{6}$	$\bar{7}$	$\bar{2}$	4	7
$\bar{5}$ *S* 11	0	$\bar{5}$	$\bar{4}$	2	5	2	$\bar{3}$	$\bar{5}$	$\bar{1}$	4	4	$\bar{1}$	$\bar{5}$	$\bar{3}$	2	5
	0	$\bar{7}$	$\overline{12}$	$\overline{15}$	$\overline{18}$	$\overline{20}$	$\overline{16}$	$\bar{4}$	10	18	12	$\bar{1}$	$\bar{9}$	$\bar{7}$	2	6
14 *S* 2	0	3	6	8	10	12	13	14	14	13	12	10	8	6	3	0
2 *S* 4	0	1	1	2	2	2	1	0	0	$\bar{1}$	$\bar{2}$	$\bar{2}$	$\bar{2}$	$\bar{1}$	$\bar{1}$	0
	0	4	7	10	12	14	14	14	14	12	10	8	6	5	2	0
Difference	0	$\bar{3}$	$\bar{5}$	$\bar{5}$	$\bar{6}$	$\bar{6}$	$\bar{2}$	10	24	30	22	7	$\bar{3}$	$\bar{2}$	4	6
Sum	0	$\overline{11}$	$\overline{19}$	$\overline{25}$	$\overline{30}$	$\overline{34}$	$\overline{30}$	$\overline{18}$	$\bar{4}$	6	2	$\bar{9}$	$\overline{15}$	$\overline{12}$	0	
	30	*29*	*28*	*27*	*26*	*25*	*24*	*23*	*22*	*21*	*20*	*19*	*18*	*17*	*16*	*15*
	y (60ths)															

Table 4. Final summations for $y = 7/60$

$$A(0, 7/60) + \sum_{1}^{H} A(h, 7/60) \cos hx - \sum_{1}^{H} B(h, 7/60) \sin hx$$

		x (30ths)															
		0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*
93	*C* 0	93	93	93	93	93	93	93	93	93	93	93	93	93	93	93	93
$\overline{26}$	*C* 2	$\overline{26}$	$\overline{25}$	$\overline{24}$	$\overline{21}$	$\overline{17}$	$\overline{13}$	$\overline{8}$	$\overline{3}$	3	8	13	17	21	24	25	26
24	*C* 4	24	22	16	7	$\overline{3}$	$\overline{12}$	$\overline{19}$	$\overline{23}$	$\overline{23}$	$\overline{19}$	$\overline{12}$	$\overline{3}$	7	16	22	24
$\overline{9}$	*C* 6	$\overline{9}$	$\overline{7}$	$\overline{3}$	3	7	9	7	3	$\overline{3}$	$\overline{7}$	$\overline{9}$	$\overline{7}$	$\overline{3}$	3	7	9
4	*C* 8	4	3	0	$\overline{3}$	$\overline{4}$	$\overline{2}$	1	4	4	1	$\overline{2}$	$\overline{4}$	$\overline{3}$	0	3	4
$\overline{10}$	*C* 10	$\overline{10}$	$\overline{5}$	5	10	5	$\overline{5}$	$\overline{10}$	$\overline{5}$	5	10	5	$\overline{5}$	$\overline{10}$	$\overline{5}$	5	10
$\overline{5}$	*C* 12	$\overline{5}$	$\overline{2}$	4	4	$\overline{2}$	$\overline{5}$	$\overline{2}$	4	4	$\overline{2}$	$\overline{5}$	$\overline{2}$	4	4	$\overline{2}$	$\overline{5}$
17	*C* 14	17	2	$\overline{17}$	$\overline{5}$	16	8	$\overline{14}$	$\overline{11}$	11	14	$\overline{8}$	$\overline{16}$	5	17	$\overline{2}$	$\overline{17}$
8	*C* 16	8	$\overline{1}$	$\overline{8}$	2	7	$\overline{4}$	$\overline{6}$	5	5	$\overline{6}$	$\overline{4}$	7	2	$\overline{8}$	$\overline{1}$	8
		96	80	66	90	102	69	42	67	99	92	71	80	116	144	150	152
$\overline{39}$	*S* 2	0	$\overline{8}$	$\overline{16}$	$\overline{23}$	$\overline{29}$	$\overline{34}$	$\overline{37}$	$\overline{39}$	$\overline{39}$	$\overline{37}$	$\overline{34}$	$\overline{29}$	$\overline{23}$	$\overline{16}$	$\overline{8}$	0
88	*S* 4	0	36	65	84	88	76	52	18	$\overline{18}$	$\overline{52}$	$\overline{76}$	$\overline{88}$	$\overline{84}$	$\overline{65}$	$\overline{36}$	0
10	*S* 6	0	6	10	10	6	0	$\overline{6}$	$\overline{10}$	$\overline{10}$	$\overline{6}$	0	6	10	10	6	0
4	*S* 8	0	3	4	2	$\overline{1}$	$\overline{3}$	$\overline{4}$	$\overline{2}$	2	4	3	1	$\overline{2}$	$\overline{4}$	$\overline{3}$	0
$\overline{33}$	*S* 10	0	$\overline{29}$	$\overline{29}$	0	29	29	0	$\overline{29}$	$\overline{29}$	0	29	29	0	$\overline{29}$	$\overline{29}$	0
9	*S* 12	0	9	5	$\overline{5}$	$\overline{9}$	0	9	5	$\overline{5}$	$\overline{9}$	0	9	5	$\overline{5}$	$\overline{9}$	0
6	*S* 14	0	6	1	$\overline{6}$	$\overline{2}$	5	4	$\overline{4}$	$\overline{4}$	4	5	$\overline{2}$	$\overline{6}$	1	6	0
		0	23	40	62	82	73	18	$\overline{61}$	$\overline{103}$	$\overline{96}$	$\overline{73}$	$\overline{74}$	$\overline{100}$	$\overline{108}$	$\overline{73}$	0
Difference		96	57	26	28	20	$\overline{4}$	24	128	202	188	144	154	216	252	223	152
Sum		96	103	106	152	184	142	60	6	$\overline{4}$	$\overline{4}$	$\overline{2}$	6	16	36	77	
		30	*29*	*28*	*27*	*26*	*25*	*24*	*23*	*22*	*21*	*20*	*19*	*18*	*17*	*16*	*15*

x (30ths)

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THE MAGNETIC PROPERTIES OF CHROMIUM

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ABSTRACT. Pure chromium has been prepared from chromium amalgam and its magnetic susceptibility has been studied over the temperature range 90 to 620° K. The mass susceptibility is practically constant over this range, the slight departures from constancy being partially explainable by the effects of thermal expansion on the experimental results. The mean susceptibility is $3{\cdot}08 \times 10^{-6}$ e.m.u. per gram at room temperature. The effects of impurities on the magnetic behaviour of chromium, which are very pronounced in the case of samples prepared at lower temperatures, are considered in detail, and the thermal and magnetic data for this element are discussed on the basis of modern theories of paramagnetism of metals.

§ 1. INTRODUCTION

Chromium belongs to the first transition group of elements and its magnetic properties are, therefore, of considerable interest; yet a survey of the literature shows that they have been somewhat inadequately investigated. For example, the value of the susceptibility per gram given in the *International Critical Tables* is $3{\cdot}7 \times 10^{-6}$ c.c.s. units, derived from the work of Honda [1]. An examination of the curves of susceptibility plotted against H shows conclusively that the materials used were markedly ferromagnetic, and indeed the chemical analysis given in Honda's paper includes the statement that the chromium used by him contained 2 per cent of iron. This is extraordinarily large and is probably an overestimate in view of the properties we have found specimens of chromium to possess in the present investigations. Again, in Owen's work [2] the amount of iron stated to be contained in his specimen of chromium was 5·3 parts per 1000, and the value of χ is given as $3{\cdot}175 \times 10^{-6}$ in a field of 26,000 oersteds, and $2{\cdot}87 \times 10^{-6}$ when extrapolated to the value in an infinitely large field. We must conclude, then, that pure chromium has so far not been investigated. This is a little surprising in view of the manner in which chromium is so readily produced in large-scale electrolytic processes for use in commerce, but it must be remembered that such preparations contain large amounts of occluded gases, notably oxygen and hydrogen, which are inseparable from the method of manufacture, and no particular care is exercised to avoid the presence of traces of iron.

In some recent work, Bates and Reddi Pantulu [3] examined the properties of amorphous manganese and showed that this element could be prepared in a non-ferromagnetic state in spite of its well-known tendency to combine with other elements to form ferromagnetic compounds. It therefore seemed to us to be of interest

to prepare specimens of pure chromium by the same method for a survey of its magnetic properties. It is generally assumed that the preparation of chromium amalgam is much easier than the preparation of manganese amalgam, but in our work we found that the former preparation was attended with considerable difficulties, although we eventually succeeded in preparing specimens of the material which we regarded as satisfactory for the purposes of our investigations.

§2. PREPARATION OF MATERIAL

Concentrated solutions of chromic sulphate, $Cr_2(SO_4)_3.7H_2O$, were prepared from the salt obtained from Hopkins and Williams, or from green flakes of specially pure chromium sulphate obtained from Merck, or from the violet powder supplied by British Drug Houses Ltd.; the first product was found the best for our purposes. To each litre of solution 7 cm^3 of sulphuric acid was added. The solution was then electrolyzed, a platinum plate being used as anode and a pool of mercury as cathode. During the course of electrolysis the strength of the solution was maintained by the periodic addition of chromic sulphate crystals. Currents of approximately 14 A., corresponding to a current density of 1·1 A./cm^2 at the cathode, were usually passed for some 100 minutes. These produced satisfactory amalgams, but it was found that higher current-densities produced a flaking of the amalgam surface or a partial breakdown of the amalgam, apparently with the deposition of crystalline chromium, in addition to excessive heating of the solution. The latter was contained in a thin-walled glass vessel placed in a container through which cold water circulated.

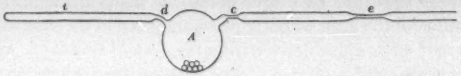

Figure 1. Apparatus for distillation of chromium amalgam.

The electrolysis was accompanied by the copious evolution of hydrogen, and slight stirring of the mercury surface was desirable. The amalgams were rather thin and quite unlike the pasty type obtained with manganese. They did, however, contain some lumps rich in chromium which were easily dispersed throughout the main body of the liquid. Now, one of the main difficulties which accompanied the handling of the amalgam lay in the fact that chromium amalgam is unstable in the presence of non-acidulated water; consequently it could not be washed in the usual manner, and it had to be washed several times with absolute alcohol for the best results, although preliminary washing with water and later washing with absolute alcohol was also tried in the case of a few preparations.

The amalgam was introduced into the bulb of the pyrex glass apparatus shown in figure 1, which is somewhat similar to that employed in the earlier work, but the present design was made for the more efficient handling of large volumes of amalgam and their subsequent treatment. The vessel was first evacuated through a short piece of new rubber pressure tubing which was then clipped, detached from the pump, and provided with a funnel whose exit tube was suitably narrowed. The funnel was lined with filter paper, and when the amalgam was placed in it, any residual alcohol

or slight impurity formed by washing came to the surface. The clip was opened and the amalgam stirred slowly as it trickled into the apparatus, impure portions being effectively shut out by closing the clip at the proper time. All these operations were carried out as quickly as possible, and, in our view, the success of the preparation depends upon the rapidity with which they are performed. The apparatus was then speedily connected to a Hyvac pump through a cooled vessel, in which mercury could condense, and drying tubes; liquid-air traps and a mercury-vapour pump were later brought into use.

The mercury was at first boiled off fairly rapidly, for in this way any film of oxide on its surface was carried over into the condenser. In the early experiments the temperature was not raised above 400° C., and when the removal of mercury had been as far as possible completed the glass apparatus was sealed at the constriction *c*, figure 1. The bulb *A* now contained the several pyrex glass beads and a mass of chromium. This mass was exceedingly hard and its pulverization with the glass beads was practically impossible; the bulb *A* was therefore broken and the substance readily powdered with a glass rod and introduced into a new apparatus similar to that of figure 1. This was evacuated with a mercury-vapour pump and heated to about 400° C. for about three hours. The powder was then forced into the tube *t* through the constriction *d* which was afterwards sealed. This was the mode of preparation of specimens similar to no. I. It should be mentioned that when the bulb *A* was broken, some slight pyrophoric action between the air and the traces of powdered chromium inside occurred, but there was no trace of such action with the main mass of the specimen which we used in our measurements. Measurements made with specimens like no. I showed that the temperature 400° C. was not sufficiently high to remove all traces of mercury and hydrogen occluded during electrolysis. The effects of such occlusions will be described below. In later experiments we therefore raised the temperature of the bulb *A* and its contents to 500° C. and maintained it for four hours. It was also found that when the temperature was raised to 500° C. the chromium yield was easily powdered *in situ* without the necessity of breaking the bulb *A*. In this way specimens like no. IX were prepared, and we are therefore disposed to regard such specimens as the purest obtained. It was usually found convenient to seal the apparatus at the constriction *e*, and then to powder the chromium. The apparatus was next connected to the pumping system by slipping rubber pressure tubing over the seal at *e*, and, when the pumps were effectively running, connexion was made to the bulb *A* by breaking the glass at a file mark previously made near the seal *e*. The temperature of the powder was then raised, and it was found, in agreement with the work of Makariewa and Birükoff[4], that hydrogen was copiously evolved in the region of 580° C. This was the treatment given to the specimen no. IX, which was maintained at the highest temperature permissible with pyrex glass under atmospheric pressure until no more evolution of gas could be detected by means of a vacuum tester. Specimen no. IX may be regarded as reasonably free of mercury, hydrogen and oxide, and we do not think it possible with present technique to obtain a much purer specimen with this temperature treatment.

§3. MAGNETIC MEASUREMENTS

The sealed tube t containing the specimen was provided with hooks and suspended vertically from one arm of a sensitive chemical balance and measurements were made by the Gouy method. To the lower end of the tube t was attached an evacuated pyrex tube of the same dimensions, in the manner described in the previous paper by Bates and Reddi Pantulu[3]. The lower end of the specimen was thus placed in a uniform magnetic field H while its upper end was in a practically field-free space when the electromagnet was excited. The pull exerted on the specimen by the magnetic forces was then given by

H

$$mg = \tfrac{1}{2}k\alpha H^2,$$

where α is the area of cross-section of the tube t, and m the difference between the masses in the pan of the balance when the field was off and when it was on. Corrections for the magnetic effect of the air surrounding the suspended system and for the glass were avoided by the use of the lower evacuated tube.

α, m

The quantity k in the above expression represents the volume susceptibility of chromium as packed in the tube; hence, to find the mass susceptibility the packing density was found later. The absolute accuracy of the results depends on the uniformity of the cross-section α; the tubes were selected with care and measured prior to use, the value of α being finally obtained by direct measurement after removal of the chromium. Determinations of k were made over the range of temperature -183 to 350° C. For the high-temperature measurements the furnace arrangement used by Bates and Reddi Pantulu was employed, but the work was greatly facilitated by the addition of a special water jacket placed between the pole pieces to maintain the latter at a uniform temperature and to stabilize the furnace temperatures. The construction of this water jacket is shown in figure 2. It was

k

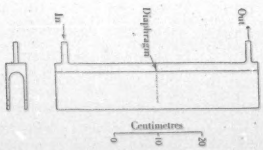

Figure 2. Diagram of water jacket for furnace.

made of thin sheet brass soldered to a frame with solid ends, as shown in the left part of the figure. The water was forced to flow evenly through the side wings by a perforated baffle around the middle, indicated by the broken line, so that the whole jacket was maintained at a uniform temperature.

For the measurements at carbon-dioxide and liquid-oxygen temperatures the specimen was suspended inside a copper tube, with a piece of rubber tubing fitted to its upper end and mounted inside a Dewar flask containing carbon dioxide snow or liquid oxygen. In one or two cases the tube was replaced by a very thick copper block which was first cooled by liquid oxygen, after which its temperature rose

slowly, and at a convenient temperature recorded by a thermocouple a magnetic measurement was taken; this was not really satisfactory and the accuracy of such measurements was not high, but they provided very valuable checks upon the results obtained at other temperatures.

§4. EXPERIMENTAL RESULTS FOR LOW-TEMPERATURE PREPARATIONS

In view of the foregoing remarks, the results obtained with specimen no. IX will be described first. In common with every specimen so far made, this specimen exhibited traces of ferromagnetism. Consequently in all our determinations we applied the Owen-Honda correction, using the equation

$$\chi_\infty = \chi_H - 2\sigma/H,^*$$

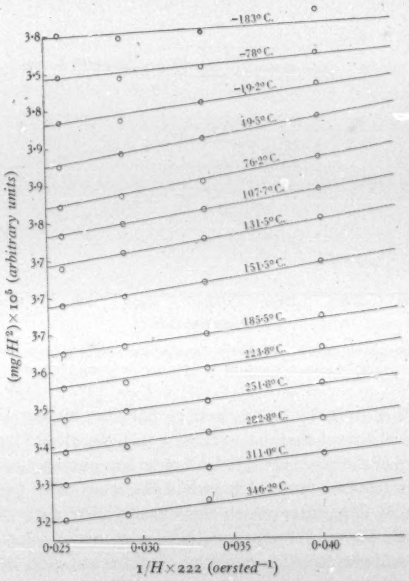

Figure 3. Specimen no. IX. Graphs showing mg/H^2, which is a measure of susceptibility, as a function of $1/H$.

where σ is the saturation specific magnetization of the impurity. A typical set of determinations is shown in figure 3, where the magnetic pull divided by H^2 is plotted

σ

* This equation is generally written $\chi_\infty = \chi_H - \sigma/H$, but in this form it can only be used with measurements in which small spherical specimens are placed in a non-uniform field, w...re $H.dH/dx$ is involved. The derivation of the correct formula for use with the Gouy method was first made by Vogt(5).

as a function of $1/H$ for a series of different temperatures. The intercept at $1/H=0$ gave the true value of the susceptibility of the paramagnetic material. It was not found necessary to apply the more complicated form of correction suggested by Vogt[5]. At the same time it should be pointed out that this assumes that the ferromagnetism is due to an impurity or rather to a compound of chromium and an impurity, and not due to pure chromium; this is a matter which will be discussed further. It is, of course, possible to obtain from the curves shown in figure 3, the magnitude of the ferromagnetic correction at each temperature.

χ

The values of χ, the susceptibility per gram of chromium for specimen no. IX, are shown in figure 4, together with the corresponding values of $1/\chi$ and the ferromagnetic correction 2σ obtained from the lines of figure 3. The value of the mass susceptibility at the room temperature is $3{\cdot}21 \times 10^{-6}$ at 20° C., which is some 10 per

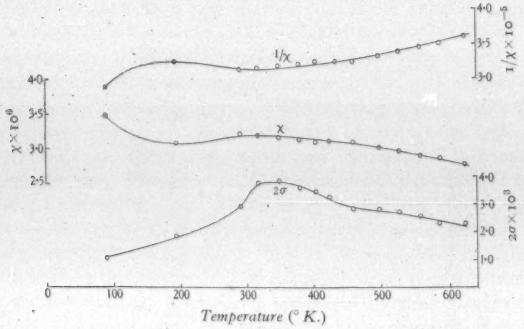

Figure 4. Specimen no. IX. Maximum temperature during preparation, 600° C. Graphs of χ, $1/\chi$ and 2σ as functions of temperature.

cent lower than that given by Honda and 10 per cent higher than that given by Owen. It will be observed that with decrease in temperature from 600° K. down to the temperature of the room there is a more or less uniform increase of χ. There then occurs a slight decrease in the susceptibility between room temperature and the temperature of solid CO_2, after which the susceptibility shows an increase. The curve of $1/\chi$ against T does not appear to call for special comment. It is obvious, however, that valuable information might be obtained at liquid-hydrogen temperatures, but these are beyond our present resources. The curve showing the variation of ferromagnetic correction with temperature is very striking, and there is no doubt whatever of the reality of the maximum there shown.

Specimen no. IV was prepared in the same way as no. IX except that the bulb A was accidentally cracked after the chromium had been powdered. The powder was placed in a tube, evacuated and heated to 620° C. for 4 hours, and then sealed. There was, therefore, the possibility that traces of oxygen and nitrogen might have had an opportunity of combining with the chromium, although precautions were

taken to evacuate the tube thoroughly before heating it. The curves of χ and $1/\chi$ are shown in figure 5 together with ferromagnetic corrections. There is some slight irregularity in the determinations, due mainly to uncertainty of correction for the ferromagnetic impurity, and it is seen that there is again a pronounced change in the paramagnetic properties as the temperature falls from that of the room to that of liquid oxygen, a change much like that found in specimen no. IX, except that there is now no sign of a decrease between $+14$ and $-78°$ C. The value of the susceptibility $3{\cdot}86 \times 10^{-6}$ at room temperature (14° C.), was also rather high.

The preparation of specimen no. I differed from that of no. IX in that occluded gases were not so thoroughly removed. The curves corresponding to figure 3 obtained with this specimen were striking in that they were parallel within the limits of experimental error for temperatures between 350° C. and the room temperature, but the

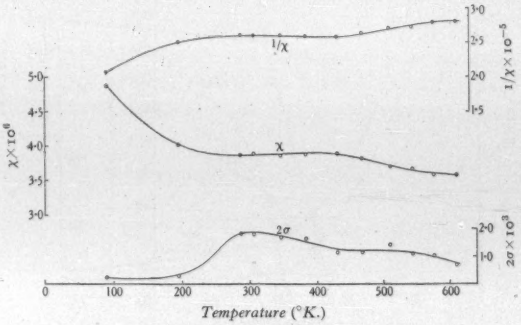

Figure 5. Specimen no. IV. Maximum temperature during preparation, 600 °C. Graphs of χ, $1/\chi$ and 2σ as functions of temperature.

ferromagnetic correction assumed rather large proportions at temperatures below that of the room. This is shown by the ferromagnetic-correction curve of figure 6, where the variation of χ and $1/\chi$ with T for this specimen also are shown. The curve of χ shows a much more pronounced rise than that which occurred in the case of specimen no. IX, and we satisfied ourselves with a copper-block experiment that the shape of the curve given in figure 6 is substantially correct. The $1/\chi$ curve shows a very marked break in the neighbourhood of 0° C. It provides a striking example of what is termed a *droite coudée*[6] or "elbowed curve", and we are tempted to enquire whether such curves really owe their existence to the presence of occluded gases in other experiments in which they have been recorded; we did not obtain such a marked break in any curve for specimens in which the hydrogen was effectively removed. The value of χ at room temperature was $3{\cdot}80 \times 10^{-6}$. The experiments so far described have been confined to specimens of chromium which have never been heated much above 600° C., and for such specimens we conclude that the most reliable value of the susceptibility at room temperature is $3{\cdot}2 \times 10^{-6}$ if they have never

been in contact with air. It is interesting that we obtained about the same values as those obtained by Honda for our less pure specimens.

The peculiarities of figure 6 are attributed mainly to the effects of traces of mercury occluded in the chromium, which give rise to much uncertainty and irregularity in the determination of the ferromagnetic correction and to the pronounced upper sweep of the $\{\chi, T\}$ curve with its associated elbow. From the other curves it appears clear that occluded hydrogen causes an increase in the value of the susceptibility, but its effect on the ferromagnetic correction could not be determined with certainty from the above experiments. The peculiar shape of the curves showing ferromagnetic correction against T was at first somewhat disturbing, but similar curves have previously been recorded by Ochsenfeld [7] for alloys of chromium with

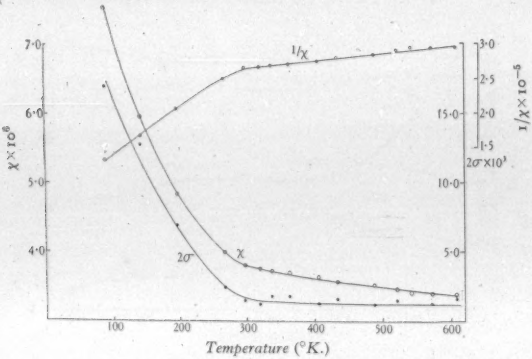

Figure 6. Specimen no. I. Maximum temperature during preparation, 420° C. Graphs of χ, $1/\chi$ and 2σ as functions of temperature.

tellurium giving compounds Cr_3Te, CrTe, and $CrTe_2$; these curves are reproduced in figure 7, and it is seen that a pronounced maximum occurs in the case of CrTe. It is unfortunate that Ochsenfeld did not extend his magnetic measurements to temperatures below that of the room. It may be suggested that as oxygen and tellurium are in the same column of the periodic table the ferromagnetism of our specimens may be due to traces of a compound of chromium and oxygen. We felt, however, that it is much more likely to be due to a combination of chromium with hydrogen and this view we think is supported by the experiments described in §5 below.

The effects of traces of mercury on the properties of chromium were brought out in the study of specimen no. III, which was not heated above 370° C. in the preliminary treatment. Starting at a temperature of −183° C. and proceeding to 350° C., the susceptibility remained practically constant. Yet between 320° C. and 350° C. disturbances became apparent, the first results could not be repeated, and with decrease in temperature from 350° C. down to room temperature a constant

increase in susceptibility was recorded; below this the susceptibility somewhat decreased. In these measurements the ferromagnetic correction remained constant and small. The specimen was now heated to 580° C. with the empty end of the tube projecting beyond the furnace. A globule of mercury condensed in this end and was removed by sealing off and detaching a portion of the tube. Magnetic measurements were then reproducible, but the ferromagnetic correction, which was of the type shown in figures 4 and 5, was enormously increased; the maximum value of 2σ, which occurred at approximately 30° C., was $4{\cdot}2 \times 10^{-2}$ per gram. Thus this

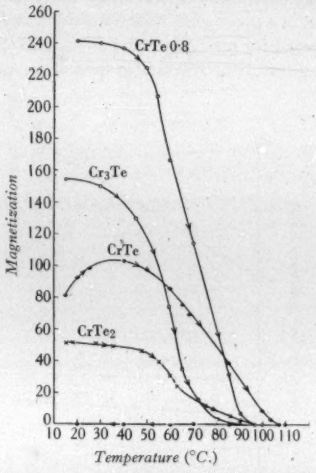

Figure 7. Ochsenfeld's curves showing variation of magnetization with temperature for compounds of chromium and tellurium.

specimen had associated with it a ferromagnetism at least twenty times as great as that obtained with specimen no. IX in the above experiments, as a result, no doubt, of the replacement of mercury by occluded hydrogen. It was therefore considered essential to evacuate the tube containing the specimen thoroughly during the high-temperature treatments described below, in order to remove all traces of hydrogen and mercury.

§5. EXPERIMENTAL RESULTS FOR HIGH-TEMPERATURE PREPARATIONS

The material of specimen no. IX was placed in a quartz tube and kept at 800° C. for four hours while the tube was continuously evacuated. The tube was then sealed and allowed to cool slowly to room temperature, and the susceptibility of the material was then determined by the above method; absolute values were not found.

The curve 1 of figure 8 shows the results obtained and there is no doubt that the ferromagnetic correction has enormously increased. The same tube was replaced in the furnace and maintained at a temperature of 1000° C. for two hours, further evacuation now being impossible. After cooling slowly the susceptibility was redetermined and curve 2 of figure 8 shows that the ferromagnetic correction had decreased to a remarkable extent; this decrease became even more marked when the specimen was heated to 1200° C. for about two hours, and curve 3 was found. The specimen now had the appearance of a sintered rod, and on breaking it up a bright grey powder—a pleasing contrast with our former black specimens—was obtained. The powder was placed in a pyrex glass tube, evacuated and heated to 450° C., and after it had been tempered for nine hours at 350° C., susceptibility measurements were made in the usual way. The relevant graphs of χ_H against $1/H$ are given in figure 9*a*.

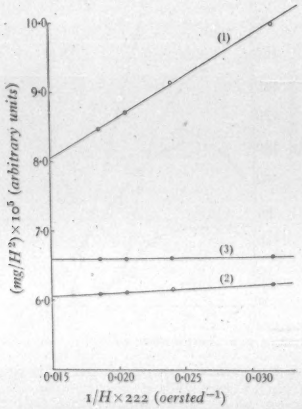

Figure 8. Specimen no. IX after high-temperature treatment. Graphs of mg/H^2, which is a measure of susceptibility, as a function of $1/H$, to show magnitude of ferromagnetic correction. Curve (1), after heating to 800° C. for four hours. Curve (2), after further heating to 1000° C. for two hours. Curve (3), after further heating to 1200° C. for two hours.

A most interesting feature of the behaviour of the specimen was that the ferromagnetic correction 2σ was much smaller and practically constant within the limits of experimental error for all temperatures between $-183°$ C. and $+350°$ C., so that we feel justified in regarding it as due entirely to iron, presumably contained originally in the chromic sulphate and introduced by the electrolysis. It is commonly supposed that it is difficult to introduce iron into mercury, but that is not our experience; in any case the presence of iron to the extent of about two parts in one million of chromium would be sufficient to account for the results now described. It is considered that an X-ray examination of the material of no. IX before and after high-temperature treatment should be of interest, and this will shortly be undertaken.

The curve showing $1/\chi$ against T, figure 9*b*, curve 2, indicates that over a range of temperature from about 35° C. to 350° C. the susceptibility obeys a Curie-Weiss relation of the form

$$\chi = C/T + \Delta$$
$$= \frac{2{\cdot}254 \times 10^{-2}}{T + 6650}.$$

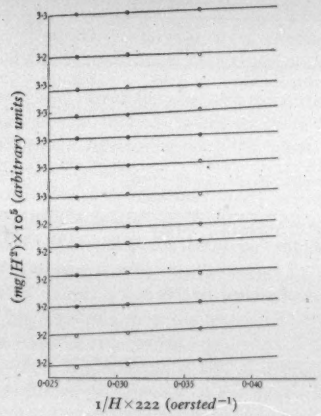

Figure 9*a*. Specimen no. IX after final high-temperature treatment. Graphs showing mg/H^2, which is a measure of susceptibility, as a function of $1/H$.

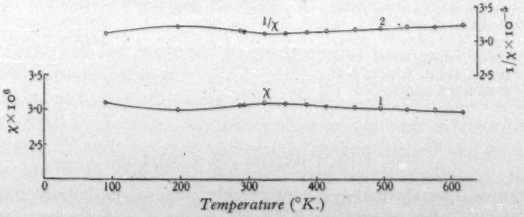

Figure 9*b*. Specimen no. IX. Final results after high-temperature treatment (at 1200° C.). Graphs of χ and $1/\chi$ as functions of temperature.

Below 35° C. the susceptibility shows a rather peculiar fall which may be due to a change in structure, or possibly to an imperfect correction for the ferromagnetism of the specimen, but the latter error is unlikely. Our final result is that susceptibility of the purest chromium so far obtained is $3{\cdot}08 \times 10^{-6}$ e.m.u. per gram or $160{\cdot}3 \times 10^{-6}$ per gram-atom at 20° C. uncorrected for diamagnetism of the core. The accuracy of this absolute value was limited by the accuracy with which the packing density could

be found. To provide the usual basis of discussion, the final experimental values of χ shown in figure 9*b*, curve 1, were corrected for the diamagnetism of the core of the chromium atom by the addition of $0{\cdot}127 \times 10^{-6}$ e.m.u. per gram[8], and the reciprocals of these corrected values are given in curve 2 of figure 9*b*.

To facilitate discussion the treatment and properties of the several specimens are summarized in table 1.

Table 1

Specimen	Treatment	$\chi_{15} \times 10^6$	Curve	Remarks
I	Maximum temperature 400° C.	3·88	Fig. 6	Contained traces of mercury and hydrogen. Large ferromagnetic correction of peculiar type (1)
III	Maximum temperature 370° C.	(Not reproducible)	—	Ferromagnetic correction constant and small
	Heated to 580° C. in evacuated sealed tube	4·78	—	Large ferromagnetic correction with maximum at about 40° C.
IV	Maximum temperature about 600° C.	3·86	Fig. 5 (Fig. 3)	Contained hydrogen. Ferromagnetic correction with maximum value at about 40° C. type (2)
IX	Maximum temperature about 600° C.; specimen completely prepared *in vacuo*	3·18	Fig. 4	Contained hydrogen only. Ferromagnetic correc- of type (2) with maximum at about 60° C.
	Specimen no. IX heated to 800° C. in evacuated quartz tube, and, after sealing, heated to 1200° C.; finally powdered, transferred to a pyrex tube, which was evacuated and sealed	3·06	Fig. 8, (Fig. 9*a* and 9*b*)	Free from hydrogen and mercury. Ferromagnetic correction small and constant over wide temperature range

§6. DISCUSSION OF RESULTS

The value of Δ for chromium is considerably higher than that obtained by Bates and Reddi Pantulu for manganese. To some extent it is dependent on the value assumed for the diamagnetism of the atomic core, for if we take no account of this we find the Curie constant and Δ to be respectively $1{\cdot}928 \times 10^{-2}$ and 5870. On the other hand, if we take the higher value 17×10^{-6} e.m.u. per gram-atom, assumed by Sommerfeld and Bethe[9] for the diamagnetism of the core, we find $2{\cdot}623 \times 10^{-2}$ and 7310 respectively. However, as the representation $\chi = C/T + \Delta$ is purely formal, it need not be discussed further.

Now, it has been assumed in the above work that no changes occurred in the packing density of the specimen or in the area of cross section of the tube. Actually,

as the temperature of the specimen is raised the material must expand and the packing density be decreased. Disch [10] has measured the coefficient of linear expansion of chromium over a wide range of temperature, and his results are given in table 2.

Table 2

Temperature, T	−78	100	200	300	400	500	° C.
Mean coefficient of expansion $\times 10^6$, between 0° and T°	0·73	0·84	0·875	0·91	0·94	0·97	deg. $^{-1}$

From these figures we should expect the observed volume susceptibility to increase with fall in temperature and the increase to become more pronounced below 0° C. However, Disch mentions the interesting point that while chromium contracts on cooling until the temperature reaches about −183° C. it expands on further cooling to −190° C. Thus while the contraction per metre between +20 and −183° C. was 1·25 mm., that between +20 and −190° C. was only 1·00 mm. Disch states that the latter values are not accurate, for the chromium surface became deformed at liquid-air temperatures and precise measurements by the Fizeau interference method were impossible. The expansion and magnetic data appear to be in close accord, except that the magnetic measurements indicate that the expansion on cooling begins before −183° C. is reached.

The thermal expansion of chromium is also of interest in connexion with the special features of the curves of figures 4, 5 and 6, for it is concluded that the presence of hydrogen has a pronounced influence in the region where anomalous expansion is found. This is, of course, in agreement with the well-known influence of hydrogen on the magnetic properties of iron [11]. It may safely be assumed that the hydrogen makes possible an exchange interaction between the electrons responsible for the magnetic properties of chromium, and so accounts for the observed ferromagnetism and the increased paramagnetism of the specimen and its pronounced temperature changes.

The expansion makes somewhat uncertain the comparison of our experimental results with those expected on the theory of paramagnetism developed by Pauli [12] and by Frenkel [13], and discussed by Sommerfeld and Bethe [8] and in considerable detail by Stoner [14]. This theory gives the following expression for $(\chi_A)_e$, the resultant paramagnetic susceptibility of the quasi-free electrons in one gram-atom of the metal when the temperature T is less than $1{\cdot}157 \times 10^4\, V_0$,

$$(\chi_A)_e = 32{\cdot}1\,(q/V_0)\left\{1 - 6{\cdot}11 \times 10^{-9}\left(\frac{T}{V_0}\right)^2\right\} \times 10^{-6},$$

where q is the number of quasi-free electrons per atom and V_0 is the width of the energy band, or the maximum electron energy in the completely degenerate state, expressed in equivalent volts. Neglecting the second term in the above expression and substituting $(\chi_A)_e = 3{\cdot}20 \times 10^{-6} \times 52{\cdot}01$, we find $V_0/q = 0{\cdot}2$ volt, while the value estimated by Sommerfeld and Bethe using other data is 0·34 volt. These values are too low, so that it may reasonably be assumed that several electron-energy bands

overlap and thus make the effective number of energy states greater. For example, if it is assumed that five energy bands, corresponding to the five energy states of the *d* electrons overlap, then the calculated values of V_0 become five times as great as those above. Or we may say that the density of states at the top of the Fermi distribution is much larger than it would be for free electrons, or that positive interchange interaction effects occur, or that both these factors are effective.

It is of interest to compare the temperature-variation required by the above theory with that found in our experiments. Thus we find $\chi_A = 3{\cdot}198 \times 10^{-6} \times 52{\cdot}0$ at 293° K. and $3{\cdot}098 \times 10^{-6} \times 52{\cdot}0$ at 619° K., when no correction is applied for expansion but correction is applied for diamagnetism of the core. If we take the coefficients of linear expansion of chromium and pyrex to be 9·7 and $3{\cdot}0 \times 10^{-6}$ per degree respectively, then the value of the atomic susceptibility at the latter temperature when corrected for expansion is $3{\cdot}119 \times 10^{-6} \times 52{\cdot}0$. Hence

$$\Delta(\chi_A)/\Delta T = 0{\cdot}0126 \times 10^{-6}.$$

The theoretical value is $-32{\cdot}1\,(q/V_0^3)\ 6{\cdot}11 \times 10^{-9} \times 2T \times 10^{-6}$, whence taking $T = 450$ approximately, $q = 6$ and $V_0 = 1{\cdot}2$ volts, we get the value $0{\cdot}000613 \times 10^{-6}$. The experimental value is therefore some twenty times as great as the theoretical value, on the assumption that $q = 6$. Lower values of q would give an approximate agreement, and, indeed, are possible, since it is only the electrons in unfilled (or partial) bands which contribute to the susceptibility. Moreover, the equation used above is based on the assumption that the energy-distribution of states of the q electrons in the unfilled band is of the same type as that for free electrons, and this may not be an adequate basis of discussion.

§7. ACKNOWLEDGMENTS

The magnetic measurements were made with an electromagnet constructed with a grant kindly made to one of us by the Government Grants Committee of the Royal Society. We desire to extend our cordial thanks to Mr H. Terrey for advice on the chemistry of chromium and to Prof. E. N. da C. Andrade for the many facilities afforded us.

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THE MAGNETIC PROPERTIES OF AMALGAMS

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ABSTRACT. The magnetic susceptibilities of a series of amalgams of known concentrations of bismuth, chromium, copper and manganese with mercury have been studied at room temperature, the Gouy method of measurement being employed in all cases. A study of the drop-weight method of measuring susceptibilities showed it to be quite unreliable for measurements with amalgams. In dilute amalgams manganese was found to possess an apparent atomic susceptibility of $+13{,}7000 \times 10^{-6}$, bismuth $+133 \times 10^{-6}$, chromium $+23 \times 10^{-6}$ and copper about $-7{\cdot}3 \times 10^{-6}$ e.m.u. All metals so far studied which are diamagnetic in the solid state are paramagnetic in dilute amalgams, with the possible exception of copper.

§ 1. INTRODUCTION

It is somewhat remarkable that in spite of its importance to the theory of the metallic state and to the theory of magnetism in particular, no systematic survey of the magnetic properties of the alloys or amalgams of mercury with other elements has been made. It is still more remarkable, however, that the generally accepted value for the susceptibility of the element mercury itself is now known to be seriously in error. The experiments described below were undertaken to supply some information concerning the magnetic properties of those amalgams which were of more immediate interest to us in connection with other work, but the opportunity was taken to redetermine the susceptibility of pure mercury and to examine certain special features of amalgams.

The value given for the mass susceptibility of pure mercury in the *International Critical Tables* (1926) is $-0{\cdot}19 \times 10^{-6}$ e.m.u. per gram, a value derived from the work of Honda [1] and of Owen [2], who both used the Curie translation method of measurement. The values of susceptibility in different fields show quite clearly that in Owen's experiments the mercury contained some form of ferromagnetic impurity, but Honda states that iron could not be detected in the specimen of Kahlbaum mercury used by him, and the observed susceptibility was independent of the field-strength. Honda's value was $-0{\cdot}193 \times 10^{-6}$ e.m.u. per gram. Owen eliminated the effects of the ferromagnetic impurity by means of the relation*

$$\chi_\infty = \chi_H - \frac{\sigma}{H} \qquad \text{.....(1),}$$

where χ_∞ is the true value of the susceptibility in a very large field, χ_H the experi- χ_∞, χ_H

* This equation is correct for measurements by the Curie method. Vogt has pointed out that σ must be replaced by 2σ when measurements are made by the Gouy method.

mental value obtained when a field H is employed and σ is the saturation magnetization per gram of the ferromagnetic impurity present. Owen states that his Kahlbaum specimen of mercury contained less than 0·0001 per cent of iron, and his measurements indicate that σ was of the order of $0{\cdot}06 \times 10^{-3}$ c.g.s. unit per gram; the value for χ_∞ is given as $-0{\cdot}184 \times 10^{-6}$ at 20° C.

It is surprising that these values have been accepted for so long without comment; in fact, until the susceptibility of liquid and solid mercury was redetermined by Vogt[3] in the course of his work on the magnetic properties of single crystals of pure mercury, the value then obtained being $-0{\cdot}168 \times 10^{-6}$ at 20° C. Vogt obtained this value by comparison of the susceptibility of mercury with that of water; and it is confirmed by our experiments. It is therefore unfortunate that his work appears to be unknown to the compilers of physical tables more recently published. Turning now to the work on magnetic properties of amalgams, only two published papers are known to us. The first, by Gnesotto and Binghinotto[4], quoted in the *International Critical Tables*, deals with amalgams of bismuth and mercury. The second is by Davies and Keeping[5], who worked with dilute amalgams of gold, tin, indium, and gallium with mercury. In addition, we find a statement by Bhatnagar and Mathur[6] that dilute liquid amalgams of copper are merely mechanical mixtures of the two metals in which the value of the magnetic susceptibility varies from that of pure mercury to that of pure copper. However, all these workers were satisfied that the correct value of the susceptibility of pure mercury was $-0{\cdot}190 \times 10^{-6}$. Davies and Keeping checked this value by comparison with pure water and state that they obtained the value $-0{\cdot}189 \times 10^{-6}$. Bhatnagar and Mathur, it is true, made no direct statement concerning the susceptibility of mercury, but the value recorded in their tables is $-0{\cdot}19 \times 10^{-6}$. We therefore conclude that the results so far obtained with amalgams are qualitative only, although some of them are certainly of interest. It is felt that the main reason for the errors found in the above measurements lies in the comparison methods used. In general it was not possible to make the series of measurements required for the application of the Owen-Honda correction, equation (1), and thus to see what part ferromagnetic impurities played.

§ 2. METHOD

In view of the facts outlined above it was considered essential to employ a direct or absolute method for measuring the susceptibility in the experiments now described. The apparatus is shown diagrammatically in figure 1. It consisted of the uniform pyrex glass tubes A and B which were suspended as shown from one arm of a sensitive chemical balance. The upper tube contained the mercury or amalgam under investigation, while the lower was evacuated. As both were cut from the same piece of pyrex tubing they were practically of the same cross section, and the lower tube acted as a compensator for the magnetic effects of the air displaced by the glass and liquid. They were connected together by a short piece of fine copper wire, and their adjacent ends were situated in the uniform magnetic field between the pole pieces NS of an electro-magnet of convenient design[7]. Let us suppose that

the magnetic pull on the apparatus for a field H is δm_0 when A is evacuated, $\delta m_a + \delta m_0$ when A is filled with air, and $\delta m_0 + \delta m_{Hg}$ when A is filled with mercury. Then the usual Gouy formula may be used for the magnetic force on a column of mercury surrounded by air, viz.

δm_0, δm_a
δm_{Hg}

$$(+\delta m_{Hg} - \delta m_a).g = \tfrac{1}{2}(k_{Hg} - k_a).\alpha.H^2 \quad \ldots\ldots(2),$$

g

where α is the area of cross section of the mercury in the tube and k_{Hg}, k_a are the susceptibilities of mercury and air respectively. In like manner, when the tube A contains amalgam with susceptibility k_{am}, we have

α
k_{Hg}, k_a

$$(\delta m_{am} - \delta m_a).g = \tfrac{1}{2}(k_{am} - k_a).\alpha.H^2 \quad \ldots\ldots(3),$$

whence

$$k_{am} = k_{Hg} - \left(\frac{\delta m_{Hg} - \delta m_{am}}{\alpha.H^2}\right).2g \quad \ldots\ldots(4).$$

In the last equation k_{Hg} and in general k_{am} are negative. It will be noted that, provided the value of k_{Hg} is accurately known, the susceptibility of an amalgam may speedily be measured by finding the difference between the magnetic forces on pure mercury and the amalgam for a chosen value of H. The field H was measured with a Grassot fluxmeter which was calibrated by measuring the magnetic pull on a solution of nickel chloride of known susceptibility.

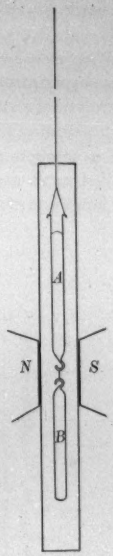

Figure 1. Arrangement for measurement of magnetic susceptibilities of amalgams by the Gouy method.

§ 3. PREPARATION OF MATERIALS

The mercury used in the present experiments was prepared as follows. After prolonged bubbling with air the mercury was washed in dilute nitric acid, in a dilute solution of potash and in water, and was finally dried. It was then distilled in a quartz vacuum still, so that all heavy metal impurities were removed. To ensure the removal of lighter and more volatile metals the mercury was redistilled in a form of apparatus like that described by Hulett[8] in a stream of air at a pressure of about 25 mm. of mercury. The amalgams were usually prepared by electrolysis, although in some cases they were prepared by mechanical mixing. The purest materials available were used, and magnetic tests were always made for the presence of ferromagnetic impurity. Details of the individual preparations are given below.

§ 4. EXPERIMENTAL RESULTS

Mercury. The volume susceptibility of mercury at 18° C. was first found. The values of the $(+\delta m_{Hg} - \delta m_a)/H^2$ are plotted against the corresponding values of $1/H$ in figure 2, from which the value of $(k_{Hg} - k_a)$ was found to be $2{\cdot}303 \times 10^{-6}$, whence, taking the volume susceptibility of air as $0{\cdot}031 \times 10^{-6}$ and the value 13·565 for the specific gravity of mercury at 18° C., the value of the mass susceptibility of mercury is $-0{\cdot}1675 \times 10^{-6}$ e.m.u. per gram, which is in excellent agreement with the

value found by Vogt. The results shown in figure 2 prove conclusively that ferromagnetic impurities were not present in this mercury. The value $0{\cdot}168 \times 10^{-6}$ per gram or $2{\cdot}284 \times 10^{-6}$ per cm^3 is taken as correct throughout the following work.

Manganese amalgam. As manganese amalgams were of special interest to one of us, experiments were first made with them. The amalgams were prepared by electrolysis of a solution of manganese chloride, a cup of mercury forming the cathode and a platinum plate the anode. The latter was surrounded by a porous pot filled with a solution of manganese sulphate. The amalgam was quickly washed in distilled water and poured into the tube *A* which was then placed in a desiccator. The latter was evacuated through drying-tubes, and by violent shaking the amalgam

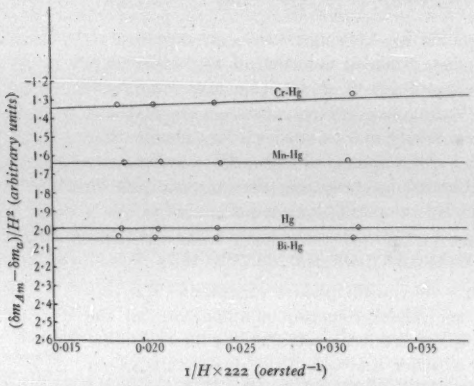

Figure 2. Graphs of observed susceptibility, plotted against $1/H$ to give the correction, if any, for ferromagnetic impurity.

was freed from water and air bubbles. On account of the small percentages of manganese used in these experiments, and because some manganese is deposited on the anode as MnO_2, the amount of metal present in a given amalgam was always determined directly by colorimeter measurements. A small known mass of the amalgam was dissolved in nitric acid, and a little silver nitrate was added. Ammonium persulphate was added to the liquid and on boiling the usual permanganate colour resulted. The liquid was made up to a known volume on cooling and its colour compared with that of a standard solution of known manganese content, using a Bausch and Lomb colorimeter. The individual concentration measurements are not highly accurate, because of the well-known limitations of such measurements.

The susceptibility measurements are shown in figure 3 where the volume susceptibility is plotted against percentage concentration by weight of manganese in the amalgam. The mass susceptibilities may be obtained by dividing the values in

figure 3 by the density of mercury, since the density of the amalgam containing 0·0257 per cent of manganese was 13·547 g./cm.³ Two tangents have been drawn to this curve, and the slope of that passing through the value for pure mercury gives the variation of susceptibility with concentration of amalgams of very low manganese content. The slope in question is considerably greater than that of the tangent drawn to the curve at higher concentrations. This is an interesting feature and is in accord with other experiments on manganese.

If we consider that m g. of a metal of mass susceptibility χ_M are amalgamated with $(100-m)$ g. of mercury, giving an amalgam of volume susceptibility k_{am} and density ρ, we may write

$$100\, k_{am}/\rho = m.\chi_M + (100-m)\,\chi_{Hg}.$$

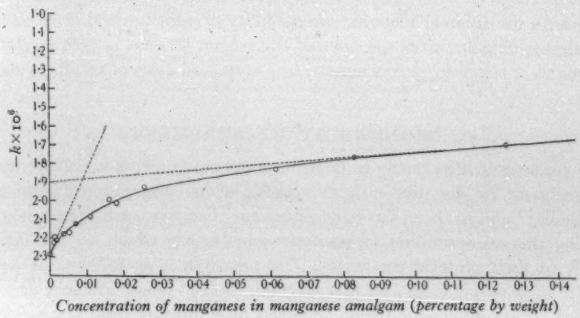

Figure 3. Magnetic susceptibility of manganese amalgams.

On differentiating and rearranging the terms, we have

$$\chi_M = \frac{100}{\rho}\frac{dk_{am}}{dm} + \chi_{Hg},$$

from which the atomic susceptibility of the metal may readily be found. In this calculation it is assumed that the metal does not combine with the mercury to form a new compound. If, however, one atom of the metal combines with n atoms of mercury to form a chemical compound whose magnetic susceptibility is χ_C, then the above equation becomes

$$\chi_C = \frac{100}{\rho}\frac{1}{1+n.M_{Hg}/M}\frac{dk_{am}}{dm} + \chi_{Hg},$$

where M_{Hg} is the atomic weight of mercury and M that of the metal; χ_C is therefore less than χ_M, and this should be remembered in discussing the properties of amalgams of high concentration.

From the slope of the first tangent we find that the molar susceptibility of manganese in very dilute solution in mercury is about $13{,}700\times10^{-6}$; in view of uncertainty in the concentration measurements the value is not regarded as very accurate.

It is, however, interesting to note that it agrees with the results obtained by other workers for dilute solutions of manganese in other metals, which are contained in table 1.

Table 1

Alloy of manganese in:	Atomic susceptibility of manganese × 10^6	Authors
Aluminium	+ 1,600	Auer[9]
Copper	13,400	Néel[10]
Silver	11,300	Néel[10]
Copper	13,400	Valentiner and Becker[11]
Mercury	13,700	Bates and Tai
Manganese (pure)	648	Bates and Reddi Pantulu[12]

The value for the differential atomic susceptibility of manganese in more concentrated amalgams obtained from the slope of the second tangent is $+674 \times 10^{-6}$. The amalgams were tested for ferromagnetic impurity, and a set of results is shown in figure 2.

§ 5. DROP-WEIGHT MEASUREMENTS

It is convenient here briefly to describe some experiments which we made on these amalgams by the drop-weight method, which was originally devised by Athenasiadis[13] and has been shown by Abonnenc[14] to give a satisfactory method of comparing the susceptibilities of solutions and liquids which do not differ too markedly in their physical properties. The principle is as follows. A liquid is allowed to drop slowly from a jet in a magnetic field H whose gradient dH/dx in a downward direction over the region occupied by a forming drop is considerable.

m, m' If the mass of each drop in the absence of a magnetic field is m, then the mass m' in the presence of the field will depend upon the magnitude of the magnetic force which will either pull the drop downwards or assist in its support. It is easy to show that, provided the surface tension of the liquid remains constant, the relation between m and m' is given by

$$\chi_l - \frac{k_a}{\rho} = \left(\frac{m-m'}{m'}\right) g \Big/ H \cdot \frac{dH}{dx} \qquad \text{.....(5),}$$

χ_l where χ_l is the mass susceptibility of the liquid. It was felt that as this method automatically avoided the necessity for density-measurements, since the term k_a/ρ is very small, and as it appeared that very small quantities of the material would be required, it might be used with advantage for determinations made with amalgams of manganese where large changes of χ_l were expected, and actually many such measurements were made before the Gouy method was employed. In our view, the work showed that the method is of very limited application, that only very dilute amalgams can be used in it, and that it is definitely unreliable in the case of manganese. The apparatus used is shown diagrammatically in figure 4, where the jet J was placed between the shaped pole pieces P of an electromagnet. The mercury or the amalgam was placed in the glass apparatus A shown in the lower portion of the figure, and by pressing the valve bulb B the liquid was forced into the tube J'

which was placed in position around the jet J. The length LL of capillary tubing, about 0·75 mm. in bore, was constricted at C, in the manner adopted in apparatus designed by Iredale[15] for the determination of the surface tension of mercury. The horizontal portions of LL were in the same horizontal plane as the orifice of J, and the end of the tubing remote from the field was bent as shown so as to be covered by the mercury in the reservoir R, which could be raised by the movable stand S. The end E lay below the orifice J, and when it was connected by rubber tubing to a water pump, the liquid under investigation could be sucked into LL with ease. The level of the mercury in R was previously adjusted to maintain the liquid in position. It will be noted that measurements were confined to the amount of liquid contained in LL, whose total length was about 80 cm. J' was then removed.

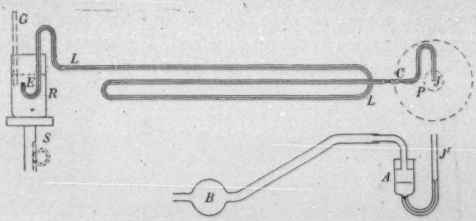

Figure 4. Apparatus for use in determination of magnetic susceptibility of amalgams by drop-weight method.

The following procedure was adopted. The liquid was forced out of J by lowering the glass plate G into the reservoir to give a higher initial head of mercury, and when the drop was nearly formed G was removed, and the final stages of the drop-formation were slowly assisted by raising the table S. Three drops were allowed to fall into a collecting vessel X when the field was not excited; then the field was switched on and three drops were collected in a vessel Y in the cases when pure mercury was used. When an amalgam was used a drop was also allowed to fall into a vessel T between the foregoing collections. Several such series of drops were collected and weighed and the corresponding values of m and m' were found. The drops in the vessel T were used in concentration-measurements as described above. To prevent oxidation of the amalgams and consequent change in weight, the vessels X and Y contained a little paraffin oil.

The constrictions C were very necessary to reduce the rate of drop-formation, but unfortunately only relatively dilute amalgams could be passed through them even when the constrictions were so wide that the rate of the drop-formation was too high. Yet the values of the ratio $r=(m-m')/m$ for pure mercury taken on successive days with the same field current were surprisingly constant, as is shown in table 2.

Table 2

$m-m'$	0·2240	0·2235	0·2253	0·2236	0·2235	0·2252	0·2245 g.
r	0·06645	0·06630	0·06676	0·06628	0·06647	0·06718	0·06697

Such differences as are observed could easily be due to field-changes. If we first use pure mercury in the apparatus, we have

$$\chi_{Hg}-\frac{k_a}{\rho}=\left(\frac{m-m'}{m'}\right)_{Hg}.g/H.\frac{dH}{dx}=(r)_{Hg}.g/H.\frac{dH}{dx},$$

and on using an amalgam we have in like manner

$$\left(\chi_{am}-\frac{k_a}{\rho}\right)=\left(\frac{m_1-m_1'}{m_1}\right)_{am}.g/H.\frac{dH}{dx}=(r)_{am}.g/H.\frac{dH}{dx},$$

so that

$$\left(\chi_{am}-\frac{k}{\rho}\right)=\left(\chi_{Hg}-\frac{ka}{\rho}\right)(r)_{am}/(r)_{Hg} \qquad \text{.....(6).}$$

The results of measurements made by this method are shown in figure 5, where the pronounced peak is very striking. We are confident that this peak properly represents the results obtained by the drop method. The value for the susceptibilities of amalgams whose concentrations lie to the right of the peak are definitely much

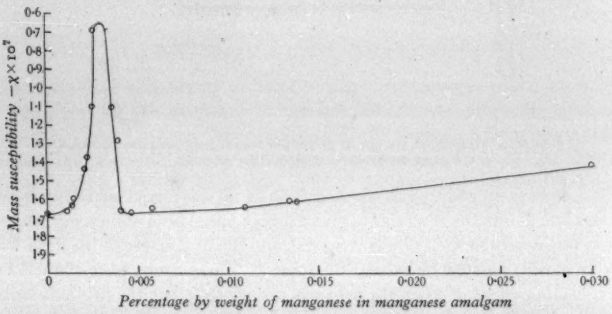

Figure 5. Magnetic susceptibility of manganese amalgams obtained by the drop-weight method. The pronounced peak is regarded as incorrect and as showing that the drop-weight method is unreliable for amalgams.

lower than those obtained by the Gouy method, although at much greater concentrations than those shown in the figure the agreement between the results was more satisfactory; but it was only by good fortune that isolated values at high concentrations could be obtained by the drop-weight method.

The presence of the peak caused much concern until we found that Royce and Kahlenberg[16], in their study of the electrode-potentials of manganese, recorded that manganese formed a saturated but very dilute solution in mercury containing only 0·0032 per cent of manganese, throughout which solid Mn_2Hg_5 was dispersed. This is precisely the concentration at which the peak occurs in figure 5. The success of the drop-weight method depends upon the constancy of the surface tension of the fluid both in and out of the magnetic field. The curve in figure 3 indicates that the dilute solution is more paramagnetic than the solid Mn_2Hg_5, so that on the application of the field the lumps of the latter should tend to leave the upper portions of the drop

and the surface tension would thereby be changed; it is considered that such changes would be at their maximum when the saturation limit is reached and should decrease as the amount of Mn_2Hg_5 increased. This, of course, does not mean that we have discovered that a magnetic field directly affects the surface tension of a fluid, for then it would also affect adsorption processes, and the circumstances in the case of these amalgams clearly do not approximate to those of homogeneous solutions. The phenomenon is interesting but leads to no definite theoretical deductions. It may be noted in passing that to explain the peak on the above lines the apparent surface tension of the drop must be increased by the presence of the field.

Bismuth. Bismuth amalgams were prepared by the complete denudation of a solution containing a known quantity of pure bismuth nitrate and a trace of mercurous nitrate, a known quantity of mercury being used as cathode and a platinum foil as anode, with a fairly high current. The weaker amalgams were quite fluid

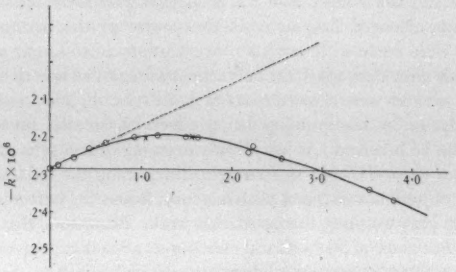

Figure 6. Magnetic susceptibility of bismuth amalgams.

⊙ Amalgam obtained by electrolysis.
× Amalgam obtained by mechanical mixture.

but the more concentrated ones showed a tendency to solidify. The percentages of bismuth were calculated on the assumption that all the bismuth in the electrolyte solution was sent into the mercury and the denuded solution was always tested with H_2S for the presence of the metal before electrolysis was discontinued. The amalgams were placed in the tube *A* and evacuated as described above. Bismuth amalgams are relatively easy to handle as they oxidize but slowly, and the same mercury can be used for several electrolytic depositions.

The curve showing volume susceptibility against concentration is drawn in figure 6. The initial increase in susceptibility was rather unexpected, but its correctness was checked by further measurements on amalgams made by mechanically mixing pure metallic bismuth with mercury, the two sets of results being in very good agreement. The points marked as crosses on the curve were obtained with mechanically mixed amalgams. The tangent at the origin of the curve shows that bismuth enters into dilute solution in mercury as if it possessed an atomic suscepti-

bility of $+133 \times 10^{-6}$ instead of -293×10^{-6}. The final slope of the curve corresponds to an atomic susceptibility of about -182×10^{-6}, although, owing to the tendency of the amalgam to solidify, this value is not considered to be of high accuracy; these figures are calculated on the assumption that the mass susceptibility is equal to the volume susceptibility divided by 13·51, the specific gravity given for a 1-per-cent amalgam of bismuth and mercury in the new edition of Landolt-Bernstein's tables.

At first sight it might appear that the peculiar shape of the curve in figure 6 is due to the presence of impurities in the bismuth, but this is not likely to be the case, for the amount of impurity should be directly proportional to the amount of bismuth introduced in the electrolysis preparations, and hence if bismuth really gives a linear relation it should persist. Moreover, we had good agreement with the check determinations carried out upon amalgams made with solid bismuth, and the bismuth line in figure 2 shows that no ferromagnetic impurity was present. Indeed, the appearance and the behaviour of the amalgams were most satisfactory, and as the mercury was changed frequently in the course of the determinations, and measurements were made with various concentrations in different portions of the curve at intervals some days apart, the curve must be regarded as well established. In addition, some samples were allowed to stand in the tube *A* for as long as forty hours without any change in susceptibility being observed, so that no change due to lapse of time can be involved. As has already been mentioned, the graph shown in the *International Critical Tables* is a straight line joining the values taken for the susceptibilities of pure bismuth and pure mercury, but as the latter value is in error by some 13 per cent we must disregard this work. Moreover, the melting-point diagram[17] for amalgams of bismuth and mercury shows a distinct phase change at a concentration of about 5 per cent of bismuth, which is outside the range of our experiments, and a pronounced change in susceptibility would certainly be expected there as well.

If, however, the large diamagnetism of bismuth can be attributed to the existence of large electron orbits which enclose many atoms in the solid state, as has been suggested by Ehrenfest, then a more ready explanation of part of the initial changes shown in figure 6 arises. For these orbits must be expected to disappear when bismuth enters the liquid state and thus the sudden decrease in diamagnetism from -213 to $-16{\cdot}7 \times 10^{-6}$ per gram-atom of bismuth on melting would be explained. In like manner, the large electron orbits would be expected to disappear totally in very dilute amalgams, but some traces of them might appear as the concentration of bismuth and the noticeable tendency to solidification increased. However, the experiments show that bismuth in low concentration behaves as a paramagnetic, and the disappearance of the large orbits is not sufficient to account for all the initial changes observed. A different explanation of the great susceptibility of solid bismuth has recently been given by Jones[18], who examined the Brillouin zones of energies occupied by loosely bound electrons in alloys with a γ structure, and showed that the lowest group of energy levels is filled by a number of such electrons in accordance with the Hume-Rothery rule. These electrons account for the large

diamagnetic susceptibility of these alloys, and Jones deduces by analogy that the existence of a Brillouin zone in solid bismuth, containing just five electrons per atom, accounts for the high value of the susceptibility, and its disappearance may account for the paramagnetic behaviour of bismuth in the amalgam. It would be interesting to carry out experiments to determine the {susceptibility, concentration} curve at different temperatures, particularly for dilute amalgams, and this we propose to do in the near future.

Chromium. The properties of chromium amalgams were of interest to one of us because they were used in the preparation of specimens of metallic chromium whose magnetic properties were recently investigated. These amalgams present rather complicated problems. In the first place, chromium amalgams break down rapidly in the presence of water, so that they had to be washed as quickly as possible in absolute alcohol before being placed in tube *A*. In this process some decomposition of the more concentrated amalgams was bound to occur, and there was evidence that the product of the decomposition, a black powder which floated on the mercury surface, was slightly ferromagnetic. In the second place it was most inadvisable to use a particular sample of mercury for more than one chromium electrolysis; the amalgams decomposed on standing in contact with air, although we reduced this effect to a minimum by placing a little oil on the surface in the tube *A*.

The amalgams were prepared by complete electrolysis of solutions of $Cr_2(SO_4)_3.7H_2O$, supplied by Hopkins and Williams, to which a little free sulphuric acid was added; the disappearance of colour indicated that electrolysis was complete. A heavy current had to be passed for some hours to obtain the largest concentrations used in these experiments, the vessel containing the electrolyte being cooled by an air-blower; it seems practically impossible to obtain higher concentrations by the electrolysis method. With chromium salts there is always a danger of iron being present; actually our specimens seem to have been fairly free from this impurity, as was shown by experiments on the chromium prepared by distilling off the mercury. The chromium line of figure 1 shows that some ferromagnetic impurity was present, and it was attributed to the products of decomposition referred to above.

The results are shown in figure 7, and it is seen that the curve consists of two parts, although this division is attributed to partial decomposition of the amalgam. The results were obtained with amalgams whose appearance was very satisfactory, for when decomposition was observed to be present the observed susceptibilities were erratic, particularly in the transition region. The chromium line of figure 1 refers to the point *A* on the curve in figure 7, and it is found that even when full weight is given to the point corresponding to the lowest field in applying the Owen-Honda correction for ferromagnetism, the calculated value of the susceptibility is changed only slightly, to *B* in figure 7.

The tangent to the curve at the lowest concentrations which showed no traces of ferromagnetism shows that chromium in dilute solution behaves as if it possessed an atomic susceptibility of $+23\times10^{-6}$ units, as compared with the value 160×10^{-6} recently found by Bates and Baqi for the solid metal.

Copper. The following experiments were carried out on copper because we

wished to satisfy ourselves that the statement that amalgams of copper and mercury are merely mechanical mixtures was correct. The greatest difficulty was found in obtaining pure copper, and all the copper amalgams we were able to make must have contained iron. We first electrolysed solutions of Analar copper sulphate crystals certified to contain less than 0·015 per cent of iron, but all the amalgams of concentration greater than 2 per cent of copper showed very pronounced ferromagnetism.

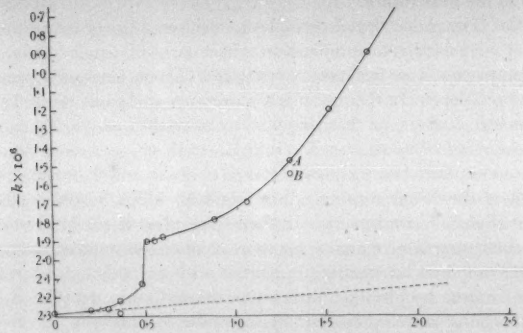

Figure 7. Magnetic susceptibility of chromium amalgams.

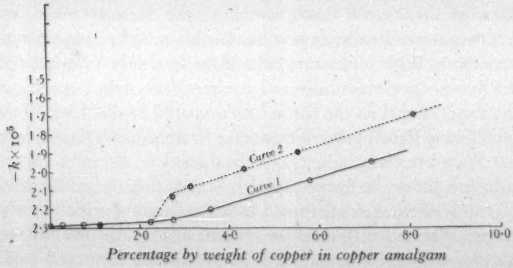

Figure 8. Magnetic susceptibility of copper amalgams. Curve 1, amalgam containing least ferromagnetic impurity. Curve 2, amalgam obtained from electrolysis of solution of electrolytic copper dissolved in sulphuric acid.

We next made solutions of pure electrolytic copper dissolved in nitric acid, but these, too, were unsatisfactory, and our most satisfactory results from the point of view of ferromagnetic impurity were obtained by dissolving copper, provided by Johnson and Mathey for analytical purposes, in nitric acid.

In curve 1 of figure 8 are shown the values of the volume susceptibility of copper amalgams obtained with the last kind of solution. The curve showing mass susceptibility against concentration is very similar because the density of an amalgam

containing 8 per cent of copper was found to be 13·494 g./cm.^{3} Hence it is clear that, with our amalgams at any rate, there is no sign of the linear relation which mere mechanical mixtures of copper and mercury would require, except in the case of very dilute amalgams where copper enters into solution with a susceptibility of about $-0{\cdot}12 \times 10^{-6}$ e.m.u. per gram. The magnitude of the ferromagnetic corrections may be gauged from the Owen-Honda lines for the more concentrated amalgams shown in figure 9.

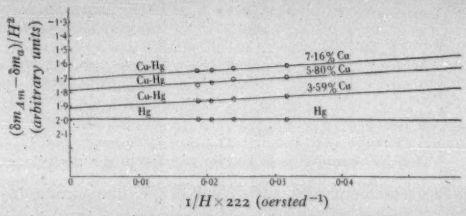

Figure 9. Copper amalgams. Graphs of observed susceptibility plotted against $1/H$ to give the correction for ferromagnetic impurity.

It is of interest to consider the effects of more pronounced ferromagnetic impurity found in the case of the second kind of solution, that of pure electrolytic copper, which has been described above. Some results were obtained by direct comparison of the magnetic forces acting on the several amalgams with that on mercury, the Gouy method, with a maximum field of 11,800 oersteds, being used. The values for more concentrated amalgams lie on a straight line, curve II, which almost passes through the point corresponding to pure mercury, but again the values for the weak amalgams lie on the initial portion of curve I. It appears that the ferromagnetic nature of iron in the mercury is only effective when a certain concentration is exceeded. This is a point of some interest to us and we propose to investigate the magnetic properties of iron, nickel, and cobalt in mercury in a separate research. When ferromagnetism is present there is always an ill-defined region between the initial and final portions of the curve II where the transition from one branch to the other occurs. This seems to be a characteristic of ferromagnetic impurity, and we have already mentioned its occurrence in the experiments on the chromium amalgams.

§ 6. DISCUSSION OF EXPERIMENTAL RESULTS

In table 3 are collected the values for the atomic susceptibilities of metals in dilute solution in mercury. The values for gallium, gold, indium and tin have been obtained from the results of Davies and Keeping[5] by use of the equation

$$(\chi_M)_A = M.\left\{100.\left(\frac{d\chi_{Am}}{dm}\right) - 0{\cdot}190\right\}\frac{168}{190}.$$

The factor 168/190 is introduced because these workers took the mass susceptibility

of mercury to be $0{\cdot}190 \times 10^{-6}$ instead of $0{\cdot}168 \times 10^{-6}$, but its introduction does not materially affect the conclusions to be drawn from the table.

Table 3

Metal	$(\chi_M)_A \times 10^{+6}$	
	In the solid state	In amalgam
Mn	+648	+13,700
Cr	+160	+ 23
*Sn	+ 3	− 10
Cu	− 5·4	− 7·3?
*In	− 16·3	+ 218
*Ga	− 16·7	+ 133
*Au	− 29·6	+ 194
Bi	−293	+ 133

* Results obtained from Davies and Keeping's paper.

The striking fact which emerges is that each of the diamagnetic metals, with the possible exception of copper, behaves as a paramagnetic in dilute solution in mercury. It is clear that valuable information may be obtained by studying the temperature variation of this paramagnetism, and this we propose to do. The data for metals which are paramagnetic in the solid state are too scanty to permit of deductions, and we propose to study other amalgams at room temperature. The high values for manganese and bismuth are in accord with the fact that MnBi is ferromagnetic; we also propose to examine the amalgam of manganese plus bismuth.

The changes in magnetic susceptibility on solution, shown in table 3, are supported by the work of Skaupy[19] on the electrical conductivities of amalgams containing small quantities of dissolved metal. He refers to the well-known fact that the conductivities of such amalgams containing the metals lead, zinc, cadmium etc. are greater than that of pure mercury, whereas the conductivities of solid solutions or of mixed crystals are always less than that of the solvent metal. These increases of conductivity may be attributed either to an increase in the number n of free electrons or to a decrease in the viscosity η, and Skaupy deduces that $n = A \,.\, \eta \,.\, \sigma_{am}$, where σ_{am} is the conductivity of the amalgam and A is a constant. An increase in n would clearly be found if the dissolved atoms lost electrons on solution, when a form of chemical equilibrium would exist between the dissolved metal and the mercury since both contain a common constituent, the electron. Such equilibrium would, of course, be modified by change in temperature, and for the interpretation of the magnetic results for a series of temperatures it would apparently be necessary to obtain the relevant conductivity data.

§7. ACKNOWLEDGMENTS

The magnetic measurements were in part made with an electro-magnet constructed with a grant to one of us from the Government Grants Committee of the Royal Society. We are indebted to Mr H. Terrey for much information on the chemistry of amalgams, to Prof. C. A. Lovatt-Evans for the loan of a colorimeter, and to Prof. E. N. da C. Andrade for the facilities afforded us.

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REVIEWS

The Quantum Theory of Radiation, by W. HEITLER. Pp. xi + 252. (Clarendon Press, Oxford: Humphrey Milford, 1936.) 17*s*. 6*d*. net.

This treatise gives an admirably clear and comprehensive account of the numerous physical applications of the quantum theory of radiation. Researches into the quantum theory may be broadly divided into two groups—the practical and the speculative. Both groups of researches start from the formulation of the quantum theory due to Dirac and Heisenberg. The object of the practical investigations is the direct application of this form of the theory to problems of experimental physics. The speculative investigations aim at a more complete and perfect formulation of the theory in which the number of axioms shall be reduced to a minimum and their effective range of application increased to a maximum. It is no derogation from the universally recognized genius of the authors of the contemporary form of the quantum theory to point out that the theory of the interaction of electric charges has no very satisfactory basis and that it is hardly wide enough for the thorough treatment of relativistic questions. In fact the theory of interaction is the outstanding problem of speculative quantum theory.

The present work is devoted entirely to the practical researches, although, of course, it indicates all the points at which the accepted theory is incomplete. It opens with a very welcome summary of the classical theory of radiation, which is treated so as to provide an introduction to the methods and technique adopted in the quantum theory of radiation. The author then discusses the quantum theory of the field *in vacuo* with especial reference to the uncertainty relations connecting the field strengths. The third and main section of the book deals with the interaction of matter and radiation, including processes of the first order such as emission and absorption, processes of the second order such as dispersion and the Raman effect, and processes of the third order such as the continuous X-ray emission. The two concluding sections discuss radiation processes connected with positive electrons and the penetrating power of high energy radiation.

This monograph presents the first systematic report on these important topics and it is indispensable not only for the theorist engaged in practical or speculative research, but also for the experimentalist who desires to know how far observations of interaction processes can be interpreted by the quantum theory. The book is beautifully produced and printed and there is a good index.

G. T.

Werkstoffkunde der Hochvacuumtechnik, by W. ESPE and M. KNOLL. Pp. viii + 383. (Berlin: Julius Springer, 1935.) RM. 36 (58*s*. 6*d*.).

The title of this book, which may be roughly rendered "Materials used in the High-Vacuum Industry", does not, perhaps, indicate at first sight how extremely useful it may be to the physicist engaged in practically any experimental research. The authors, who are closely connected with the great Siemens-Konzern, and thus possess special facilities and advantages for compiling a work of this kind, have assembled a body of exact information on the properties of metals, glasses and other substances, such as phosphors, used in what may be called the electrical tube industry, and on the preparation and working of those materials. A great deal of the information has not hitherto been accessible, at any rate to those outside industry, without the greatest trouble: most of it has been published, it is true, but generally in such places as the *Veröffentlichungen* of the Siemens-Konzern, the Osram-Konzern and other corporations; in technical journals which are found in very

few English libraries; or in patent specifications. The ordinary standard tables do not readily, if at all, yield the figures here given, and the standard books on applied physics are silent on most of the processes and devices. The academic and technical physicist will therefore be saved prolonged search if he requires any of the information contained in this book, and it is unlikely that he will not, in the course of his work, sooner or later have to deal with the materials of which our authors treat.

The metals handled are tungsten, molybdenum, tantalum and niobium; the platinum metals; and a group of other metals, chief among which are nickel, iron and copper, used in vacuum tube construction. There are tables for each separate metal, giving a variety of physical constants, many not usually tabulated. Alloys, mercury and the alkali and alkaline earth metals are then discussed in turn. There follows a special section on the treatment of the metals used in tube construction, dealing, for instance, with welding and soldering. The physical properties of the various glasses used are treated in detail, with full tables, and many other substances, such as mica and asbestos, are discussed in turn. Among other subjects may be mentioned the preparation of phosphorescent screens for cathode ray tubes; the various types of hot cathode; the methods of gettering; and the making of glass-to-metal joints.

The book is full of pieces of useful information. The reader will learn that quartz windows can be sealed to ordinary glass tubes by the use of suitable intermediary glasses: that the use of nickel instead of iron in sealed off tubes is largely due to the insufficient purity of iron, especially carbon contamination; he will find nomograms for obtaining true temperature from the measured "black" temperature of various surfaces, resistance of metal wires and such like; and very compact diagrammatic representation of the purification processes of various gases. The illustrations, some four hundred in number, are strongly to be commended. My only criticism is that the index is very incomplete, which makes the tracing down of particular points a little more troublesome than it need be. The book is one which I shall often open.

E. N. DA C. A.

Handbuch der Experimentalphysik, Band XVI, Teil 1. *Magnetooptik*, by W. SCHÜTZ. Pp. x + 378, with 138 figures. (Leipzig: Akademische Verlagsgesellschaft m.b.H.) Price M. 32.

This treatise on magneto-optics, from which the Zeeman effect is excluded, forms a very interesting addition to the Wien-Harms series. It is written in a most engaging style, and the clear legends attached to each figure, the careful dissection and explanation of every mathematical formula, and the precise statement of all symbols in convenient places make the work a particularly valuable book of reference. The data here published have been collected with considerable care and critical discrimination, and they are most adequately discussed.

About half the book is devoted to the theory and experimental technique of the Faraday effect, the rotation of the plane of polarization of light by passage through a medium parallel to the lines of force of a magnetic field. The arrangements of Allison and Beams are, very properly, briefly described and their findings reported. The sections on diamagnetic and paramagnetic rotations are well set forth, but that on ferromagnetic rotation is specially illuminating.

A second portion of the book, some sixty pages, is given to the discussion of magnetic double refraction. The author mentions a very simple method of showing the Voigt effect in which only a small magnet and a spectroscope which will resolve the *D* lines of sodium are required. In connexion with the Cotton-Monton effect some striking data as to the amount of double refraction of nitrobenzene observed with different electromagnets are given, and some little attention is paid to the importance of this effect in the elucidation of problems of the chemical structure of molecules.

The magneto-optics of colloids and large particles are dealt with in a third portion of some fifty pages, and the reflection of light at the surfaces of magnetized bodies in the final portion of about the same length. Throughout the whole treatment the author proves clearly that he has read widely, and that he has not confined his reading to German periodicals. The important theoretical work of C. G. Darwin, for example, is properly appreciated. The whole standard of the work is certainly as high, if not higher than that of the earlier volumes of this Handbuch.

L. F. B.

Dynamics of Rigid Bodies, by WILLIAM DUNCAN MACMILLAN. Pp. xiii + 478. (McGraw-Hill Publishing Company Ltd., 1936.) Price 36*s*.

This is the third volume of a series on theoretical mechanics by Prof. MacMillan of the University of Chicago, the titles of the two previous volumes being "Statics, and the dynamics of a particle" and "The theory of the potential". It is intended to furnish an introduction to the study of rigid dynamics, and to that end it has been made a complete and independent treatment of the subject based firmly upon Newton's laws of motion, and every chapter has been equipped with a fair number of problems. The author states explicitly that the student of rigid dynamics is expected to be well advanced in his mathematical training, and indeed this book does make considerable demands on his knowledge and abilities. The only similar work in English is Whittaker's classical treatise on analytical dynamics, with which the present volume may be justly compared both in its wide scope and in its sound and detailed treatment of the many problems of pure mathematics which arise.

The freshness and originality with which MacMillan discusses the historical problems of dynamics are perhaps best shown by an indication of the many novel features in this work. Vectorial methods are made fundamental throughout. The chapter on systems of free particles includes the permanent configurations in the problem of n attracting bodies. The discussion of motion on a fixed plane includes an elaborate discussion of the friction on a sliding base, allowing for the yielding of the plane. The treatment of the motion of a rigid body about a fixed point includes the integrable case discovered by Mme Kowaleski. The theory of the rolling and spinning of a coin on a horizontal plane is worked out completely in terms of hypergeometric functions. The concluding chapter on the method of periodic solutions gives a rigorous and detailed account of the mathematical theory, including some unpublished work of Dr W. Bartky on linear differential equations.

These brief indications will show the great width of the field covered by the author and the diligent care with which it has been intensively cultivated. This work will become a standard treatise on rigid dynamics for the advanced student and lecturer, and Prof. MacMillan has made us all his debtors by the publication of this masterly exposition.

G. T.

The Freedom of Man, by ARTHUR H. COMPTON. Pp. xi + 153. (New Haven: Yale University Press; London: Humphrey Milford, Oxford University Press.) Price: 9*s*. net, or $2.00.

In this book the author has brought together the material which was presented as certain foundation lectures in 1931 and 1935. The preparation of these lectures provided him with the incentive to formulate the relationship between his own scientific and religious thinking "much more carefully" than he otherwise would have done. The first lecture is entitled "Freedom versus Law, an Age-long Conflict"; the second lecture on "What Determines Our Actions" contains a very clear exposition of Heisenberg's uncertainty principle in language which can readily be understood by the layman. As a physicist the

author concludes in this lecture that "there is no reason from the consideration of the actions of living organisms to doubt the universal validity of the laws of physics; but these laws are insufficient to make possible an exact prediction of such actions". In the third lecture "Intelligence in the World of Nature" the hypothesis is endorsed "of a supreme Intelligence working through nature's processes as the only satisfactory method of accounting for the remarkable world in which we find ourselves". The fourth lecture "Man's Place in God's World" discusses the relation between God and man from a scientist's point of view. In the last lecture "Death, or Life Eternal" the author examines the question of immortality and concludes "that science finds itself incapable of giving a definite answer, at present at least". The statement in this lecture (p. 122) "The older Jewish teaching has little to say on the question" is open to question. We read for example in Psalm xlix "But God will redeem my soul from the grasp of the grave: for he will receive me" and again in Psalm xvi "For Thou wilt not abandon my soul to the grave; neither wilt thou suffer thy loving one to see the pit"; and yet again in Ecclesiastes, ch. x, v. 7. "And the dust returneth to the earth as it was, And the spirit returneth unto God who gave it." In addition to these few quotations there are the many ancient Rabbinical commentaries on these and similar passages which occur in the Old Testament.

For those with the desire to think beyond their "to-day" the book can be warmly recommended as an affirmation, in the light of scientific discoveries, of belief in the fundamental tenets common to the principal faiths of the world.

H. R. L.

The Science Masters' Book (Series II), Parts 1 and 2, by G. H. J. ADLAM. Part 1, pp. xvi+273. Part 2, pp. xvi+252. (London: John Murray.) Price 7*s*. 6*d*. each part.

I have often thought that it would be amusing to show how very many simple physical experiments could be performed, qualitatively and quantitatively, with apparatus ordinarily available in every household. By suitable purchases the list of experiments could be extended very considerably and if the additional apparatus were bought in the cheapest markets and instructions for making such simple instruments as the astatic galvanometer, the metre bridge, the monochord etc. were available, an interested student could equip his own private laboratory for an outlay of about a sovereign.

The laws of the simple pendulum can be demonstrated with a plum-bob, or a Newtown pippin. Pins and a convex lens (3*d*.) can be used to illustrate image-formation and to make clear the idea of parallax (the golfer should welcome this). A cocoa-tin is a satisfactory calorimeter. I am reminded of this old idea by the books under review, for in the volume on physics there are several lists of general apparatus obtainable from toy shops and stores, and here are such instructions as are necessary for their use. Altogether there are some two hundred notes and experiments, all interesting and some novel, which have been selected from the *School Science Review*, so that with those included in the first series very large fields in physics, chemistry and biology are covered in the four volumes.

One of the especial merits of a collection of notes of this kind is that of stimulating the reader to modify, and even, perhaps, to improve upon them. I had not thought of such a simple way of illustrating Lenz's law as the one described, but only a few minutes were required in which to wind two similar coils, one a closed circuit and the other open-ended, to fix them some ten inches apart and to suspend the system from a thread and carry out the demonstration. If, like myself I regret to say, you missed seeing Series 1 (1931) of these publications, your immediate reaction should be to make amends for the oversight, for these books should be in every laboratory where the above-mentioned sciences are taught.

J. H. B.

Under the general heading *Actualités Scientifiques et Industrielles* we have received the monographs listed below. Each is written by an authority on his subject and the treatment is, in general, concise and clear. The publishers are Hermann et Cie., 6, Rue de la Sorbonne, Paris.

268. Lee A. Dubridge. *New Theories of the Photoelectric Effect.* 12 fr.
269. J. J. Trillat. *La Diffraction des Électrons.* 18 fr.
278. P. Fleury. *Mesures Géométriques.* 20 fr.
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310. M. Quintin. *Activité et Interaction Ionique.* 18 fr.
312.
313.
336. G. A. Boutry. *Phénomènes Photoélectriques et leurs Applications.* Pts. 1–6. Nos. 312 & 336, 20 fr. Nos. 313, 337, 345 & 346, 15 fr.
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315. Marcel Mathieu. *Réactions Topochimiques.* 12 fr.
316. Marcel Mathieu. *La Nitration de la Cellulose.* 12 fr.
317. Marcel Mathieu. *La Gélatinisation des Nitrocelluloses.* 12 fr.
321. C. Musceleanu. *Chaleur Spécifique et Théorie des Quanta.* Parts 1 & 2. No. 321, 15 fr. No. 322, 12 fr.
322.
324. P. Lainé. *Biréfringence Magnétique.* 15 fr.
330. René Arditti. *Les Théories Quantiques.* 8 fr.
344. E. Darmois. *Le Deutérium ou Hydrogène Lourd.* 10 fr.

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 48, PART 6 *November* 1, 1936 NO. 269

530.1

PHYSICAL ULTIMATES

BY PROF. F. A. LINDEMANN, M.A., PH.D., F.R.S.

The twenty-first Guthrie Lecture, delivered on May 15, 1936

I WILL commence by telling you a little fable.

ERRATUM

"The density and coefficient of expansion of liquid gallium over a wide range of temperature", by W. H. HOATHER, M.Sc., A.Inst.P., *Proc. phys. Soc.* **48**, 699 (1936).

In the footnote on p. 705

for page 704 *read* page 703.

particular. On the other hand, he was assured that if he integrated round a contour roughly 2 in. broad and 1 in. deep round each dot, he would be pretty safe in assuming these areas contained 1 unit.

"Why", he asked, "must I do this?"

"Obviously", was the reply, "to take account of the boundary conditions."

"Why is it", he asked, "that the dots so seldom are close together?"

"Clearly", was the reply, "because of the exclusion principle."

"But here", he pointed out, "are two of them quite close together."

"Ah, but these", he was told, "obviously have opposite spins."

"At any rate", he said, "if I promise to observe all these rules, can I rely upon your map?"

"Well, not exactly," was the reply, "for however accurately we make our observations, by the time we have drawn the map and go back to check it up, we always find the dots are in the wrong places."

"What is the use of that sort of map to me?" he said.

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The twenty-first Guthrie Lecture, delivered on May 15, 1936

I WILL commence by telling you a little fable.

There was once an earnest enquirer interested in sociological problems, more especially those connected with the distribution of population. Like most earnest sociologists he had little knowledge of human beings and dealt mainly with tables and maps. The maps from which he got most knowledge and profit used the convention that a given number of population units was represented by a small dot. The density of the dots could be correlated with all sorts of other quantities, height above sea-level, rainfall, etc., and our earnest enquirer found them of enthralling interest. On his smaller maps on a scale of 10 miles to the inch, each dot of course had a hundred times the weight of each dot on his larger maps drawn on a scale of 1 mile to the inch. As his studies progressed our enquirer demanded larger and larger maps until finally special maps on a scale of 1 foot to the inch were prepared for him by the Royal Cartographical Society.

When he went to fetch these maps he received rather a shock. A lower limit, he was told, existed to the importance which could be attached to a dot. Nor must he assume that the position of the dot indicated the presence there of anything in particular. On the other hand, he was assured that if he integrated round a contour roughly 2 in. broad and 1 in. deep round each dot, he would be pretty safe in assuming these areas contained 1 unit.

"Why", he asked, "must I do this?"

"Obviously", was the reply, "to take account of the boundary conditions."

"Why is it", he asked, "that the dots so seldom are close together?"

"Clearly", was the reply, "because of the exclusion principle."

"But here", he pointed out, "are two of them quite close together."

"Ah, but these", he was told, "obviously have opposite spins."

"At any rate", he said, "if I promise to observe all these rules, can I rely upon your map?"

"Well, not exactly," was the reply, "for however accurately we make our observations, by the time we have drawn the map and go back to check it up, we always find the dots are in the wrong places."

"What is the use of that sort of map to me?" he said.

"Well", said the cartographers, "we have made whole bookfulls of maps and by careful study we have found a correlation between the probable place of the dots and the right ascension and declination of the sun and all sorts of other rules such as the probability of finding a large number congregated together when one dot disappears or when two coalesce. We cannot of course guarantee anything but if you apply these rules you will find that you have a pretty good chance of predicting the right result."

"But what is it all about?" asked our earnest enquirer, "and why have we to give up our old, simple conventions which I could understand and which worked so well?"

The cartographers looked at him with shocked disapproval.

"What on earth is the good of asking a ridiculous question like that? We have given you a set of rules which will tell you anything that can be told and all that any respectable enquirer ought to wish to know."

So our student was thrown back upon his own resources. He took his maps home and pondered over them and finally came to the conclusion that a human being could not be subdivided and that the boundary conditions merely represented the fact that his projection in plan covered some 2 ft. by 1; that the exclusion principle arose from the fact that no two could occupy the same space, though occasionally, if their spins were of opposite sign one sat upon the other's knee. That they moved about and had definite habits such as going to the City in the day-time and home to bed at night and that they tended to congregate at funerals and marriages. But when he went and told the cartographers this they told him to go to a place where all maps were printed on asbestos paper.

I confess I am in great sympathy with our earnest enquirer in the fable. For something very similar has recently happened to many experimental physicists. Notoriously the methods of classical physics have proved inadequate. In their place we have been given various forms of quantum dynamics, matrices and q numbers, ψ functions and operators. All of them are elegant, original and what is more they deliver the goods. But none of them seem to claim or even wish to claim any physical basis. They are admirable, perhaps perfect rules for calculating what we shall observe, but the ordinary experimental physicist asks what has gone wrong with our classical way of looking at things. Why have we had to introduce these new forms of mathematics, what does it all mean? I will endeavour to-night to explain my view of what has happened. To do this it is necessary to go right back to the metaphysical basis of scientific research and to discuss the ultimate physical concepts or indefinables in terms of which our theories are expressed.

Philosophers seldom agree. But if there is one point upon which they are unanimous, it is that the only absolute knowledge we have or ever can have, is the knowledge of our own sense experiences. A consensus of opinion in such quarters is impressive. All of us, I imagine, will be prepared to accept the sense data as our raw material.

The task of the physicist is to codify these sense data and to work them into a coherent system.

The solipsist's position, that there is nothing beyond ourselves, that all our experiences are merely imaginary, that is to say conditioned by no external stimuli, is a tenable and indeed incontrovertible one. But the physicist is bound to reject it.

For a solipsist has no need of physics. Conversely no physicist can be a solipsist. As we have said, the solipsist's position is admittedly impregnable. So is that of the bankrupt. The physicist refuses to glory in mental insolvency.

The physicist therefore assumes, and nobody can do more than assume it, that there is something external to himself, an external world between which and his sense experiences there is some relation. His aim is to make some picture, model or map of this external universe.

It is often said that his job is merely to predict what is going to happen. This is not true. A tide machine can predict the tides. We demand more than this. We desire to relate them to something else, to fit them into our mental picture. After all, any set of recurrent events can in principle be analysed out of its context by the method of Fourier series. If we were content merely with prediction, this would be all that was required. But we are not. We have progressed from the Babylonian Saros cycle to the system of Ptolemy, from Ptolemy to Copernicus, from Copernicus to Kepler, from Kepler to Newton and from Newton to Einstein.

Man has never been content merely with noting recurrences. He wants a system, he desires to "understand"; and it is this instinct which the physicist endeavours to satisfy.

The physicist then is somewhat in the position of a man who is called upon to make a map of the globe. A certain amount of knowledge is available from past experiences. He can, and if he is an experimentalist, he should explore fresh regions himself. What his present state of knowledge about the universe is, it is difficult to estimate. As regards the physical sciences, I would suggest that it compares with that of the average yokel in Italy in the year 500 B.C. regarding the geography of the globe.

Now it is evident that whatever map the physicist makes will never be complete. No map ever can be. If it were it would cease to be a map and simply be a duplicate of the whole external world. The idea of a map, picture or model implies a certain selection. It only pretends to represent certain aspects. But between these aspects and our sense experiences we are entitled to demand a one-to-one relation.

The sense data with which the physicist is mostly concerned are the result of experiments designed for a particular purpose. A difficulty of selection in some ways analogous to that mentioned above confronts us here also. For no experiment can be exactly repeated, and some way of deciding which circumstances matter in the arrangement of the experiment has to be found. When we observe that a certain object placed twice running in the pan of a spring-balance causes it each time to descend a distance equal to a given ruler, it is quite arbitrary to state that the experiment has been repeated. In the interval the plants have grown, the observer has aged, some thousand million people have moved, the temperature has changed, electric charges have been displaced and the planets and stars have altered their positions. What warrant have we for neglecting all this?

The justification, such as it is, is instinctive. However often we carry out the experiment we observe the same result. Once, twice, or three times, one might believe that external effects might cancel one another out, but not an indefinite number of times.

How many times, it may be asked, must an experimental result repeat before we are justified in refusing to believe they have by chance neutralized one another and in coming to the conclusion that the varying external circumstances have no influence upon the observation? There is no answer to this *a priori*. It is a matter of instinct, of taste. If someone refuses to accept your estimate you can never prove him wrong; the only thing to do is to ignore him.

This instinctive criterion of course only applies to events which repeat. Many experiences, for instance those most important in our own personal history, show no tendency to recurrence. As regards these, therefore, we cannot apply the instinctive test described above. We can only appeal to "physical theory". So far as any criterion goes, the position of the stars and planets at any given moment might perfectly well influence the course of our individual lives; a claim which astrologers have maintained for millennia, not without pecuniary profit.

Thus we see that there is another justification for the physicist's endeavour to form a coherent map or model of the external universe. Not only do we derive aesthetic pleasure therefrom; it enables us to estimate what circumstances are likely to affect observations, or, at any rate, we believe it does. Most of us think this justifies us in spending our lives in trying to draw such a map or helping others to fill in its details.

We now come to the fundamental question, how shall we draw our map? What conventions shall we adopt, what co-ordinates shall we use?

In ordinary map making there are dozens of different systems, all in certain circumstances justifiable. We have one-dimensional maps like the R.A.C. route maps; ordinary two-dimensional maps with contour lines and colours, etc. indicating heights; three-dimensional "relief maps". There are maps whose contour lines indicate rainfall, density of population or geological formation, maps on Mercator's projection and on a host of other schemes. All or any of them can be justified provided there is a one-to-one relation between the map and what it is intended to represent and provided the particular convention used is clearly stated and understood.

The ordinary conventions of cartography by no means exhaust the possibilities; a map or picture is by no means the last word. A long table of figures for instance might be made to serve the same purpose. Thus for instance each row of figures could represent a small area; the first group could give the latitude, the second the longitude, the third the height above sea-level, the fourth density of population, the fifth rainfall, etc. Such a table of figures would have many advantages. An unlimited number of factors could be taken into account. The distance between any two points could be derived by a simple calculation from the first two groups of figures. The deviation from the Pythagorean formula would be a measure of the curvature of the globe. The rainfall or the population of any given region could be discovered by a simple integration. All the facts could be represented by a figure in a polydimensional space. If one were prepared to multiply one's dimensions they could all be contracted to one point in a space of sufficient complexity and the history of the whole world represented by one world line. But there would be one grave dis-

advantage. A calculation would always be required before the content of the map could be apprehended.

Despite the immense freedom and latitude all these methods of representation provide, there are certain circumstances in which they break down. One instance was described in my fable. It would be easy to name many others. But we are concerned to-night with physics.

Whilst the cartographer has at his disposal an almost unlimited set of possibilities and is allowed and indeed expected to use a different map for each quality which he is endeavouring to represent, the physicist is expected to portray everything upon the same map. This makes his task much harder. *Sub silentio*, of course, many of us do use different maps, as when we are thinking for certain purposes in terms of Euclid or Galileo rather than of Einstein. But we do not boast of doing this and indeed many of us refuse to admit it. If we have to use the same map to represent all aspects, of course, the choice of co-ordinates and conventions becomes much more difficult and important; difficult for obvious reasons; important because if one only has one map, one is apt to forget that it is merely a map and to mistake it for reality. In principle, of course, as we have said, the choice is a matter of taste. All that one can insist on is that a convention be not ambiguous and that it be clearly set forth. But the word "taste" implies a great deal. It implies that the choice commend itself to those concerned to deal with the matter, i.e. that the map be intelligible to those who have to use it. It implies by the same token, simplicity, i.e. that it involve a minimum of mental effort to understand. A book is required not a cryptogram, a dictionary not a cross-word puzzle. But even a book is no use unless we understand the language in which it is written. Some of us find some languages so hard to understand that we can only spell out the meaning of the beautiful poems which have been written in these languages and miss almost all the joy and pleasure which the authors so evidently take in them.

My purpose to-night is to plead for a translation into the vulgar tongue. I am quite convinced that the main underlying fundamental metaphysical basis of the modern quantum dynamics can be made intelligible to the average experimental physicist. I urge that this should be done. After all, very few read the Scriptures in the original Greek, even in Oxford. Far fewer no doubt than pretend they do. Most of us are prepared to sacrifice some of the lapidary clarity which we are told distinguishes the classical tongues for a sound comprehension of the language. There was a good deal to be said for the production of the Authorised Version. Can we not have one in physics?

Since none has been forthcoming from the mathematicians I venture to put a sketch before you to-night which does, I believe, explain in physical terms what is implied by the new forms of theoretical physics. The difficulties have arisen, I am confident, because we are using as our ultimate concepts indefinables which are not really appropriate to the external world we are endeavouring to describe. To make my view clear I must consider the fundamental concepts which are in current use.

In Victorian times the particular set of mental co-ordinates or physical concepts, which should be employed in our description of a physical universe, was not con-

sidered to be a matter of doubt. Space and time were taken for granted as ultimate indefinables as they had been since the time of the Greeks. The concept of mass ever since Galileo and Newton had been the third indefinable which enabled one to make a coherent picture of mechanical processes. In the course of the nineteenth century various new derived concepts were added, electric charge and potential, magnetic dipole and field and so forth. But all of these could be defined in mechanical measure once the laws governing electro-magnetic interactions were formulated. One group of concepts did not fall into line in this respect, namely those derived from the very elementary notion of temperature such as the entropy. It was only Boltzmann's brilliant and original interpretation of the entropy in terms of the kinetic theory which made this intelligible.

Many of the derived concepts of mechanics gained acceptance because their effect was so easily perceptible or because they had such primitive analogues. Our muscular reactions make us believe that we know what a force or a pull is; experience in the nursery teaches us to appreciate the idea of an impact with its correlated concept of momentum. Some derived quantities such as energy took many years to become popular. It is strange when one reads older scientific papers to realize how difficult it was for this particular concept to achieve universal understanding and recognition. Habit and use has to-day made most physicists believe that it is as familiar to them as the idea of mass or even length or time; an instructive instance of how easily it is possible by habit and use to gain the impression that one of these physical concepts is a thing we can apprehend *a priori*.

A concept of even more general application than energy is that of action. This unhappily has not penetrated our consciousness with the same success as the energy or momentum concepts. Its many definitions prove how little it has become acclimatized. Almost always we shall find that it is energy integrated over the time or the momentum over the length. Just the same questions are asked about it as used to be asked about the energy. Where does it reside; what becomes of it in a process and so on and so forth? Yet in principle, it has just as good claims as the energy to be considered an ultimate concept, especially when we remember the extraordinary generality of the law of least action which governs every process in classical physics.

Which of these various inter-linked concepts, length, mass, time, energy, action, electric charge, magnetic field, etc. should be taken as the ultimates and which as the derived concepts is a matter of taste. A great number of groups of three can be used as the ultimate indefinables and the others as derived concepts. We have no more real reason to consider length, time and mass as our natural ultimates than we have to consider cartesian co-ordinates the natural ones to use in geometry. It used to be thought that it was preferable to use co-ordinates which one could measure directly. People were under the illusion that length was one of these. But when one comes to exact analysis it is perfectly plain that a whole lot of elaborate physical theories are involved in any accurate measurement of length. The same holds good of time and mass. But if this criterion falls to the ground the apparent obvious pre-eminence of these particular concepts vanishes. Any other suitable group of ulti-

mates would have equal validity provided we could accustom ourselves to thinking in terms thereof. Thus, for instance, mass, charge and action could perfectly well be substituted for mass, length and time. The difficulty would be to get used to thinking in these terms.

Though we are in principle at liberty to choose any co-ordinates or conventions we like in our map of the external world, the aspect we elect to consider frequently renders certain initial conventions much more convenient than others. Just as in geometry no sensible person would describe a spiral in cartesian co-ordinates or a space-lattice in polar co-ordinates, so in physics it seems probable that the most natural description may be preordained by the external world of which we are endeavouring to give a picture. If the ultimates imposed by the nature of the external world happen not to coincide with those to which our mental prepossessions and habits incline us, a conflict will arise. It is this conflict in my view which found expression in what used to be known as the quantum paradoxes.

To understand this, it is necessary to examine the advantages and disadvantages of two very simple alternative modes of description which we can employ in our world map, namely, the continuous and discontinuous. In ordinary macroscopic mechanics there could be no doubt which was the more convenient. The discontinuous form of representation, the description of a system in terms of particles, positions and momenta imposed itself. In the theory of elasticity on the other hand, the continuous equations, fortified by Fourier's proof of the universal validity of harmonic analysis, were obviously the more convenient. In the case of matter the two modes of description were harmonized by admitting that every substance was composed of individual particles or molecules and confining one's applications of the continuous method to regions so large that they contained a considerable number of such molecules. Provided it was realized that the accuracy of the continuous prediction within a given region could only be absolute if it contained an infinite number of molecules, this mode of representation proved perfectly adequate.

For many generations all phenomena associated with light and radiation appeared far more apt to be described by the continuous mode than by the discontinuous. It was only the observation at the end of the last century of the immensely concentrated production of energy in the photoelectric effect which cast doubts upon its universal applicability.

This choice between the continuous and discontinuous modes of description is one of the great problems in considering physical ultimates to-day.

All our early experiences, all our mental prepossessions, almost, one may say, all our natural instincts, lead us to favour the discontinuous form of representation. From our earliest years we have learnt to recognize a lump of sugar, a toy or a stone. Whether it is a projection of our consciousness as individual entities or whatever the cause, this form of picture is so deep-rooted in our nature that it is difficult to overcome it. All space-time description is based upon it; were it not possible in principle to recognize a particle, to fix a point in space, co-ordinate systems would be hard to conceive. Thus the ordinary experimental physicist is extremely loath to adopt universally a continuous form of description of the universe. Though every

physicist would agree that it is possible to represent an atom in the old-fashioned sense, i.e. a concentration of matter, by an infinite number of waves extending to infinity in space and time appropriately arranged to conspire in any desired locality to form a large crest, very few would care to think of the world in such terms. It is this fact of experience, just as valid as any other of our sense data, which inclines us if at all possible to describe the external world in terms of particles.

In the description of ordinary matter, this convention has long been taken for granted. The atomicity of apparently continuous material may have appeared a paradox a 100 years ago, it seems almost self-evident to-day. Indeed it is the breakdown of this mode of description in its simplest form which has shaken metaphysics so severely.

In electricity the atomic mode of description is of much more recent date. As late as 1900, it was held in the German Law Courts that electricity was not a substance, but that to be electrified was a state of material substance, a decision greatly to the advantage of the ingenious individual who was acquitted of theft although he had hooked a conductor on to the overhead wires of the passing tramline company and driven a considerable workshop with the power thus abstracted. It was only since the beginning of this century, when the researches of Sir J. J. Thomson and others gave so many examples of what one would most naturally describe as its atomic characteristics, that the idea that electricity consisted of highly charged particles analogous to the molecules of ordinary matter became popular and indeed universally accepted. As electricity was later than matter to be described in discontinuous terms, so the difficulties of this mode of description were apprehended earlier. Thus diffraction and interference phenomena, so familiar from the study of light, by a somewhat ironic coincidence were observed in the case of electrons, by the son of Sir J. J. Thomson within 30 years of their discovery. Similar phenomena, of course, have since been observed in the case of atoms. We shall revert to these failures of the space-time description of the atomistic picture of the external world later.

Just as the experiments by Sir J. J. Thomson pointed almost inevitably to the necessity of describing electrical phenomena in terms of atoms of electricity, so the host of phenomena associated with the quantum theory have pointed, under the inspiration of Planck, to the necessity of describing action in atomic terms. Many of us have a great difficulty in grasping this. We think of action not as an ultimate indefinable, but as a derived concept made up of components such as momentum and length and energy and time or angular momentum and angle. It seems to us obvious that each of these components can be varied continuously and almost absurd therefore that their product should be discontinuous. But this is largely a matter of habit of mind. Potential and capacity after all can also be varied continuously or for that matter length and breadth and height of a solid body. Yet nobody allows these facts to discourage him from describing electricity and still less ordinary matter in atomistic terms. Some slight alteration in the definition of action may be necessary, possibly mainly, in order to avoid offending our prejudices, just as a certain latitude in placing the zero of energy is frequently convenient. But the desirability of treating

action as atomic, at any rate, when we are determining the course of a process by the Law of Least Action, seems indubitable.

The assumption that action is atomic causes a complete metamorphosis in our outlook. For we wish to represent the world in terms of space and time. Were we content to forgo this, we might of course, describe a hydrogen atom in the ground state simply by saying it is one proton, one electron and one atom of action. But, as has been said, our mental elasticity is insufficient for us to alter so fundamentally our concepts. The ordinary physicist insists, probably rightly, on space and time as his ultimate concepts. Atomic action forces him to reconsider the validity and indeed possibility of doing this.

Let us take the concept of space for instance. Space, like any other concept, is an invention of the human mind to deal with sense data. Sense data are given us by our experiences and are in the widest sense the result of experiment. According to the classical physics, which are, at any rate, approximately accurate, any experiment involves a process governed by the law of least action, i.e. some ascertainable amount of action occurs. In any observation of a length therefore an amount of momentum also is involved.

According to the classical way of looking at it one could plot the action integral for every conceivable mode of transition from the initial state to the final state, these two, of course, being defined by positional and momentum co-ordinates. The mode of transition which would actually be observed, would be the one for which the action integral was a minimum. Geometrically, this could be represented as a curve the lowest point of which would define the process which actually occurs.

Now if action is atomic, it is clear that this action curve will be replaced by a series of steps approximating in their general envelope to the old-fashioned curve. But one sees at once what an immense difference it makes to one's whole metaphysical outlook. For a series of steps of this nature, instead of having a minimum, has a region in which all the points have the same lowest value. Hence the perfectly definite assertion which classical physics was able to make as to the process which would be observed, is replaced by a much more indefinite statement merely giving a region within which the observed phenomena might be expected to occur. This result has effects of fundamental importance, for it implies that the old sharp four-dimensional Minkowski's world lines are degraded to rather indefinite broad and washy regions.

It has an even more far-reaching result. From the classical point of view a system required for its description the exact statement of the positional and momentum co-ordinates of every particle. But this did not rule out the possibility of stating these co-ordinates independently of one another. A concept is meaningless unless it is in principle possible to observe the quantity which it typifies. Even according to classical physics, of course, any observation implied an experiment involving a certain amount of action. Hence, in general, the observation of a length would imply that the momentum was affected and *vice versa*. But according to classical physics, the amount of action could be in principle infinitesimal. Hence either co-ordinate could be observed without affecting the conjugated co-ordinate.

If action is atomic this possibility vanishes. A finite amount of action must be involved and consequently whichever co-ordinate is observed, a finite effect must be produced upon the conjugated co-ordinate. We have said above that it is meaningless to discuss the concept of an unobservable quantity. It is equally unjustifiable, if the observation of the quantity which we are erecting into a concept implies inevitably something about any quantity which can also be regarded as a concept (i.e. the conjugated co-ordinate), to make a statement about the first quantity leaving out of account the second. Our concept of length is formed as a result of our being able to measure length. If every observation of a length implies that the particles whose position is in question must have a momentum, it is not permissible to divorce length from momentum and treat it as an independent concept. If action is atomic no observation of position is even in principle possible without momentum being conveyed to the object whose position is being measured. It follows that every statement about position implies a statement about momentum. To employ the concept of length alone, neglecting the momentum aspect of the observation on which the concept of length is founded, is logically wrong. The error caused thereby may be small, as indeed it is in macroscopic physics, but it is always in principle present and all the major quantum paradoxes have resulted from its neglect.

It should perhaps be emphasized that this point of view deviates fundamentally from that generally held. Ever since Heisenberg enunciated the Principle of Indeterminacy it has been recognized that the observation of one conjugated co-ordinate affects the other. I desire to make it plain that I go a step further than this. I maintain that since the legality of forming or using a concept depends upon the possibility of observing the quantity in question, it is absolutely illogical to endeavour to introduce as an independent concept any quantity, if it is certain that the observation thereof would imply something about another quantity. If that is so you have two linked concepts and any statement about the one implies something about the other. This is not because we have observed it or anything of that sort, it is simply because, since the quantity involved of the first concept could not have been observed without producing some effect on the quantity concerned in the second concept, we have no right to treat either of them as independent quantities and as such endow them with the status of independent concepts.

We know that conjugated co-ordinates are concepts of this type. This being so it is to my mind completely illogical to talk about, say, the distance between two objects or the energy of a system at a given moment. If one says "object A is 1 cm. from object B" one must complete the sentence "and has the probable momentum X". Similarly, if one spends a long time t in measuring the energy of a system one can say to within a great degree of accuracy that its energy is E; but it would be quite meaningless to say the energy at a given moment was E. There is no sense in stating the energy at all apart from the time. Energy *per se* is a faulty concept.

The accuracy with which the energy can be stated depends upon the length of the time available. At any given instant of time it may have any value from nought to infinity. The probable error of course diminishes as the time over which it is measured increases. But at best if it were possible to plot it as a function of the time

one would find a fluctuating quantity whose deviations from the mean might have any value.

Exactly the same considerations, of course, apply to any pair of conjugated co-ordinates. Just as a statement about the time implies a statement about the energy, a statement about the angular position implies a statement about the angular momentum. Our minds cannot use the action concept as an ultimate and we are entitled if we wish to use other concepts derived from it; but if it is impossible to represent action by a continuous expression, then no concept derived from it is valid, divorced from its conjugated concept.

The question of course at once arises: what does a statement about one co-ordinate imply about the conjugated co-ordinate? The answer obviously depends upon the type and degree of broadening to which the Minkowski's world lines are subject. At first sight, one might expect an ordinary fading out according to some form of error law. We shall see later on that this over-simplifies the problem. What is clear, however, is that a statement about one conjugated co-ordinate implied by a statement about the other conjugated co-ordinate can never be an exact statement, but can only give a probable value. It may be and, of course, is possible to state the average value, but in any given instance only the probability of observing a given result can be predicted.

The recognition of this logical necessity, namely, that any statement about one co-ordinate implies something about the conjugated co-ordinate invalidates at one stroke many of our most cherished mental prepossessions. Take, for instance, the fact mentioned above that it is no longer possible to talk of the energy of a system at a given instant of time. There is no real reason why this should offend us. We all think we know what the potential of a charged conductor is. But the potential of a conductor containing only one electron is a very indefinite quantity. All our concepts are derived from experiments made with macroscopic objects in which we are dealing with immense numbers of entities. It is scarcely surprising that they should be of their very nature statistical and that difficulties should arise when we try to apply them to individual particles.

This consideration brings us to the idea of distinguishable states. Classical physics would have endeavoured to describe hydrogen atoms in spatio-temporal terms by describing the shape and size of the orbit on which the electron moved and stating its momentum. What we have said shows that such a procedure is not only in practice, but in principle impossible. Any statement about the size or shape of the orbit automatically implies something about the momentum. A very accurate statement involves a very large momentum, often one which is much too large to be compatible with the orbit in question. Such a statement is simply devoid of sense. All we can do is to differentiate between a number of distinguishable states, defined by the condition that we can distinguish one state from the other without changing the system from one to the other. Bohr energy levels, as it turns out, are the mean values of the energy of the system in each of these distinguishable states.

The broad outlines of what we may call the major quantum phenomena all emerge automatically from this point of view. The energy in a system at the ab-

solute zero whose existence seemed so paradoxical 20 years ago becomes an obvious necessity. For we elected to draw our map in terms of particles; as we have seen, the mere fact that we can state that the particle is within the system, i.e. that its position can be stated to a given degree of accuracy, implies as the necessary corollary that it has at least a given amount of momentum and consequently of energy. The rotation of, say, a diatomic molecule equally follows as a matter of course from the mere statement that it *is* a diatomic molecule. For a diatomic molecule is a system not spherically symmetrical. The introduction into our description of the hypothesis that there is such a system is equivalent to introducing something capable of defining an angle and as a logical necessity the statement that we have something capable of defining an angle carries with it the subsidiary statement and therefore having angular momentum. The so-called quantum states are merely the various distinguishable states and the various forms of the quantum theory merely represent accurate methods for inserting into the classical theory the correction which the classical assumption, that a statement about any co-ordinate alone was possible, requires.

There is, of course, a certain logical hiatus in continuing to use classical laws, once one has realized the necessary implications produced by the atomicity of action of any statement about a co-ordinate. For the classical laws are all stated in differential form, i.e. an infinitesimal change in one co-ordinate corresponds to an infinitesimal change in the conjugated co-ordinate. As we have seen, the statement that we know any co-ordinate very accurately implies a large but uncertain value of the conjugated co-ordinate so that an equation implying that we know one co-ordinate with only an infinitesimal error involves an infinite uncertainty in the conjugated co-ordinate. Nothing therefore could be further from logical consistency than to utilize differential equations connecting two conjugated co-ordinates when we know that far from an infinitesimal change in one corresponding to an infinitesimal change in the other, the mere use of an infinitesimal in the one implies an infinite value of the other.

The classical body of knowledge, of course, was derived from experiments with a very large number of particles and represents the average effect, for a large number of individual entities are concerned. This is harmonized with the new point of view by assuming that the average result of a large number of consecutive experiments will approach the average value for a large number of particles with which the experiment is done simultaneously. Everyone will agree that the same result will be obtained by tossing a million pennies simultaneously as will be found if a penny is tossed a million times consecutively. It is this assumption that we have made in what is called the Correspondence Principle and though there is no *a priori* justification for it, nobody is likely to quarrel with it.

This line of approach of course differs decidedly from that of the mathematician. He takes the view that the form of the classical differential equations is everything and must be maintained at any cost. In order to achieve agreement with experiment he is quite prepared to alter the interpretation of the symbols and indeed their very meaning. Thus a perfectly well-defined physical quantity, which one would normally

expect to be expressible as an ordinary number representing the ratio of this quantity to one's conventional unit, is translated (in the sense of the *Midsummer Night's Dream*) into an imaginary differential operator. It would be ungracious to complain of this; it gives the right results. But unless some better reason, some explanation more intelligible to the experimentalist, is provided I shall stick to my interpretation of what the process implies.

To recapitulate, the external world appears to be so constituted that it does not lend itself to description using the ordinary ultimate concepts of physics, namely mass, length and time in the classical way, since this implies that action can vary continuously. If we insist on using these ultimates on account of our mental conservatism, then we must realize that any statement about them implies a statement about the conjugated co-ordinates and due account of this must be taken. When this is done most of what we may call the major quantum phenomena emerge. Unfortunately this is not all.

As mentioned above, it would appear natural that the connection between the probable correction to the conjugated co-ordinate necessitated by a statement about any primary co-ordinate should be given by a probability expression such as one would desire in the usual way, remembering that the elements of action along the axes are additive. This is not the case. If one wishes to obtain agreement with observation one has to substitute for the ordinary probability relation with a real exponent the same expression with an imaginary exponent. Once again, of course, one can display a lack of curiosity and interest in this result and simply say it is so. I am not at all satisfied that this is the utmost we can do. On the contrary it appears that there is an argument derived from quite a different set of experiments which makes the fact intelligible.

As we have stated repeatedly, one of the ultimate concepts most commonly used in physics and which we all believe ourselves to understand, is time. The most significant thing about time or, at any rate, about our apprehension of it, is the marked difference between past and future. Since, according to almost any description of the universe, a physicist is made up of an immense number of particles, it is natural to attribute his very definite apprehension of a direction in the time axis to physiological phenomena based on the second law of thermodynamics. For in the second law, of course, we have the determining quantity, the entropy which increases always as time goes on.

Now Minkowski 30 years ago showed that all the major equations of classical physics could be put into comparatively symmetrical form if one introduced a new variable whenever the time occurred which was simply the time multiplied by the velocity of light and $\sqrt{(-1)}$. If this were done, he showed that one could describe the external world very simply with four completely equivalent interchangeable variables, three of which were identical with the old-fashioned directions of space and the fourth represented, in the new form, the time axis. In other words, he showed that the simplest description of the external world was achieved by utilizing this new variable instead of our time. The essential difference is, of course, that the new variable corresponds to an imaginary time.

It is this fact, in my view, which explains why the relation between the conjugated co-ordinates is not given by an expression with a real exponent, but by an expression with an imaginary exponent.

We have seen above that the external universe requires for its representation something in the nature of an atomic action. It would seem from what has been said that it would be represented better still by substituting a concept analogous to action in which space and time are on an equal footing. In terms of such a concept, of course, the relation between the conjugated co-ordinates would be an ordinary probability relation such as one would naturally expect.

Owing to our mode of apprehending time, the real exponent corresponding to this probability relation would appear as an imaginary quantity. It follows that our mental need to represent events in terms of the ordinary space and time, which we have learnt to know and love in the nursery, forces a sort of wave aspect on to our apprehension of the external world. If we insist on using something akin to spatial co-ordinates, the simplest representation probably would be in terms of Minkowski co-ordinates with an atomic Minkowski action implying an appropriate error-law connection between the conjugated co-ordinates. We have already made a complication by splitting up our action; by substituting our ordinary time we introduce another. If we take account of this, however, the probability expression obviously becomes an oscillatory one and the whole wave aspect of our experience is comprehensible.

In the foregoing, I have endeavoured to give some idea of the conventions and co-ordinates which I prefer in drawing my map of the external universe. As I have said at the outset, the answer to the question which are the best conventions is entirely a matter of taste. Some people may be content with a series of mathematical expressions which they believe it is impossible to translate into physical concepts. Provided, they say, we can establish our one-to-one relation between these little black marks on a sheet of paper and our sense data we ask nothing more. They are, of course, fully entitled to adopt this attitude. For many years students of thermodynamics were content to accept Clausius's entropy without desiring to relate it to anything else. Its explanation in terms the experimental physicist could understand did not alter it, but merely enriched thermodynamics. I believe that an effort to make the quantum theory intelligible to the experimentalist is justifiable for similar reasons. As long as we are compelled to think in terms of space and time and mass and charge and energy and action, so long will the physicist demand why all these mysterious operator equations and matrices and q numbers have to be introduced. He knows that any conventions in drawing his map are permissible. He wants an explanation in terms of the concepts with which he believes he is familiar. As I have said, I believe the answer to be that the external universe is so constituted that it would be best represented by other ultimates than those which we know so well, say, mass charge and some sort of Minkowski action. In such terms perhaps we should be able to describe it, using nothing but whole numbers. But these concepts are not ones with which the experimentalist can work. He wants to use, as heretofore, his ordinary mass, length and time. If action is in any form atomic, it is obvious that

this will impose the need for a correction in the conjugated co-ordinate whenever a co-ordinate is used. Our ordinary human apprehension of time which the principle of relativity has proved long ago to be differentiated from our apprehension of length mainly by the factor $\sqrt{(-1)}$ imposes an oscillatory aspect on our observations. Once we have realized this we can see the reason underlying the more complex calculations of the theoretical physicist. We do not question their methods or their accuracy, all we want to know is what they are about. Nobody challenges the accuracy of a table of logarithms or questions the methods by which they are calculated. But nobody ought to be content when working out what he will owe his bank in 20 years' time, merely to look out the figure opposite the figure representing his overdraft and the figure opposite 1·05 to multiply the latter by 20, add the two together and look out the figure to which the result corresponds. Most of us would ask what the whole process amounts to and why it gives the right result.

The purpose of this lecture will have been achieved if it stimulates physicists to display a similar lively interest when dealing with the mathematicians. Whether such a display of curiosity will render the client popular with the directors of his bank or the physicist popular with the mathematician is of course a totally different question.

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SECONDARY EMISSION FROM COPPER DUE TO SLOW POSITIVE IONS OF ARGON

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ABSTRACT. The dependence of the secondary emission from the cathode on the energies of the impinging positive ions is of importance in the mechanism of the corona, or asymmetric, discharge through gases. In particular, it is important to find whether positive ions are able to liberate electrons from an electrode on to which they drift when their mean energy of agitation is no greater than that of the atoms of the gas through which they move. This paper describes experiments performed with positive ions of argon moving in that gas under weak electric fields in order to measure the secondary emission produced at a copper cathode. No secondary emission was detected when the electric intensity Z was less than 20 V./cm. and Z/p was less than 40, but the secondary emission attained a value of about 1·1 per cent when the electric field was increased above 60 V./cm. corresponding to values of Z/p greater than 100. This result is compared with those previously obtained with hydrogen and helium ions under similar conditions.

§ 1. INTRODUCTION

The emission of electrons from metals under the impact of positive ions plays an important part in the mechanism by which the glow discharge is maintained. The relative importance of this process and that of the ionization of the gas molecules by collision with positive ions varies from gas to gas, but it would appear that the process of secondary emissions practically always occurs to some extent at the cathode of a discharge tube.

Suppose that the average number of electrons emitted from a metal by the impact of one positive ion be called γ. It is reasonable to consider that γ in any given case can only depend on the nature of the metal, the nature of the positive ion, and its kinetic energy at impact. Now in order to derive information about the mechanism of this process it is necessary to find how γ varies with the kinetic energy of the positive ions, and also to find how it depends on the ionization potential of the atom from which the ion is formed. It has previously been suggested that the process of electron emission under positive-ion bombardment is one of electrostatic attraction of the electrons from the metal due to the electric field of the ion[1,2], and a theory based on this view has been suggested[3]. If this were the case it would follow that electron-emission could occur when positive ions arrive at the target with the smallest possible kinetic energy. Now it is well known that ions with kinetic energies greater than 100 volts can cause the emission

of electrons from electrodes, and the value of γ is known to be a function of the kinetic energy of the ions; but the effects of positive ions having much lower energies have not been studied so fully.

When the positive ions move through a gas, as in the glow discharge, their energy of agitation is, in general, some function of the ratio of the electric force Z to the pressure p of the gas. This function depends on the many processes which may occur when an ion collides with an atom, but the ratio Z/p may be taken as a suitable parameter. It is therefore important to know how γ varies with the values of Z/p near the cathode, if the conditions obtaining in discharge tubes are to be reproduced as much as possible. The knowledge of the dependence of γ on Z/p when Z is low is important, again, if a consistent theory of the asymmetric discharge is to be formulated.

In the work described in this paper the values of the coefficient γ were measured for copper with positive ions of argon moving through the gas under electric forces between 20 and 90 V./cm. when $Z/p < 150$.

§ 2. DESCRIPTION OF THE APPARATUS

The apparatus, illustrated in figure 1, comprised three circular discs A, B, and E of thin copper 4 cm. in diameter with cylindrical rings round their edges, and two semicircular copper plates C and D 3·5 cm. in diameter and 0·5 mm. thick. The electrodes were supported and insulated from one another on four pyrex rods not shown in the figure. The distance between the discs A and B was 1·7 cm., and

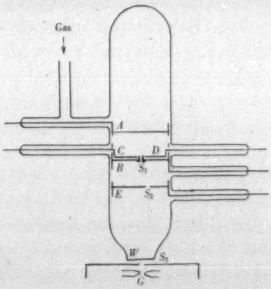

Figure 1. The magnetic field is perpendicular to the plane of the paper.

between E and B 2·25 cm. The electrodes C and D were 0·5 mm. from the disc B and were insulated from it by thin plates of pyrex. The whole was enclosed in a pyrex cylinder so that the surfaces of electrodes were perpendicular to the axis of the cylinder.

There was a slit S_1 at the centre of the disc B 1·25 mm. wide and 9 mm. long, while the disc E contained a slit S_2 2 mm. wide and 9 mm. long, situated 0·5 cm. off its centre. The edges of these slits were parallel to the straight sides of the

semicircular plates C and D. The slit S_1 was fitted with a lip so arranged that the beam of positive ions was not intercepted by the plates C and D. Connexions to the electrodes were taken through tungsten-pyrex seals in the side tubes. The end of the tube was fitted with a quartz window W by means of a pyrex-quartz graded seal. This window allowed ultra-violet light from the spark G to pass through the slit S_2.

The apparatus was evacuated by means of a mercury-vapour diffusion pump backed by a Hyvac oil pump, and the pressure was measured by means of a McLeod gauge. A liquid-air trap was fitted between the tube and the pumping and measuring apparatus, to prevent mercury vapour from diffusing into the apparatus.

The gas system consisted of a reservoir of commercially pure argon, a pyrex tube containing palladium black, a tube containing charcoal, and two quartz tubes containing metallic calcium. The first quartz tube was fitted with an electric heater so that the calcium could be kept at a red heat in order to absorb impurities from the argon. The second quartz tube was interposed between the last greased tap and the pyrex tube containing the apparatus; and it was sealed to it by means of quartz-pyrex graded seals. The purpose of the calcium in this tube was to prevent the diffusion of any vapours from the tap grease into the apparatus. Repeated heating of this tube was sufficient to maintain the gas quite pure over long periods.

§ 3. EXPERIMENTAL PROCEDURE

The gas used in these experiments was allowed to stand over the palladium black for some time in order that the hydrogen which is present in the commercially pure argon might be absorbed. The charcoal tube served as a pump to circulate the argon over the red-hot calcium, a method due to McCallum and Klatzow[4].

The glass parts of the gas system and the charcoal were thoroughly degased by heating them up to 300° C. for long periods with the pumps evacuating. Both tubes of calcium were kept at a red heat until they gave off no gas at this temperature.

The apparatus containing the electrodes was wound with an electric heater and kept at 360° C. for a week while the tube was kept evacuated in order to take the water vapour out of the glass. After this, the apparatus was further heated to a high temperature by means of a blow pipe, and also by maintaining a discharge between the electrodes and afterwards pumping out the gas. Care had to be taken in this operation as copper sputters very easily.

The light from the spark G passed through the slit S_2 and fell on to the underside of the electrode B and liberated photoelectrons, which were accelerated to the plate E by the electric field between E and B, and so ionized the gas. The positive ions were attracted to the plate B and some of them were drawn through the slit S_1 by the field between the plates A and B. The light was limited to a narrow beam by a slit S_3 in the screen surrounding the spark gap, so that no light from the spark gap entered the apparatus except through the slit S_2. The position of the beam of light on the plate B was so adjusted that no direct light passed through the slit S_1,

and it was found that in a certain critical position the light scattered through the slit S_1 was negligible. The potential between E and B was so arranged that a positive-ion current of sufficient intensity was received by the plate A. This potential was found to be about 10–20 V. less than the sparking potential between B and E.

The action of the positive ions after passing through the slit S_1 was determined by measuring the negative current received by the electrode C which was at the same potential as the electrodes D and E, and comparing it with the positive-ion current received by A.

The electrodes B, C and D were kept at earth potential and A was maintained at a negative potential V, so that the positive ions passing through the slit S_1 moved towards the disc A under a force Z equal to $V/1{\cdot}5$, the distance of A from the electrodes C and D being 1·5 cm. The surfaces of the plates C and D and the edge of the slit S_1 were all coplanar so that the field Z was sensibly uniform except at the edges of the electrodes. The connexions to the electrodes were all protected from leakage over the glass by external guard rings only, as it was found that owing to the length of the side tube (10 cm.) internal guard rings were unnecessary.

When the force Z was sufficiently large, electrons were set free from the electrode A. These electrons were deflected by means of a uniform magnetic field maintained in the whole of the space between the electrodes A to E by two large coils on either side of the pyrex cylinder. The deflected beam of electrons fell on the plate C or on the plate D when the field was reversed. Owing to the very high value of the lateral diffusion of the electrons in argon, it was found to be impossible to deflect the whole of the beam on to C. By reversing the magnetic field it was found that at the optimum field-strength 10 per cent of the electrons was received by the other plate D. A correction was applied to all the values of the electron currents received by the electrode C, and in order to allow for all possible losses of electrons an addition of 15 per cent was made to the observed electron current. The optimum magnetic field was that field which gave the maximum ratio of the electron current received by the plate C to the positive-ion current received by A.

The negative charge received by C, and the positive charges received by the plate A, were measured by means of an electrostatic balance comprising a sensitive electrometer connected to screened air condensers and a potentiometer, and so arranged that the potentials of the electrodes did not alter during the measurements. It was found that for the critical position of the spark G the electrodes C and D received no charge when the potential between E and B was small, say 20 V., and a strong field maintained between A and the electrodes C, D. Such charges would have been due to diffused light entering the space AB. Hence this shows that no charge or ultra-violet light entered the space between A and B unless positive ions were produced by ionization in the space between B and E. Moreover, when the positive ions passed through the slit S_1, to fall on A, no positive charge was intercepted by either of the electrodes C, D. The positive-ion currents passing through the slit S_1 were of the order of 10^{-10} A.

§ 4. THE EXPERIMENTAL RESULTS

The measurements were carried out for values of Z from 10 to 90 V./cm. corresponding to values of Z/p less than 180, for which the mean energies of the positive ions in argon have been measured and are known to be low[5]. The low values of Z/p were obtained by using low values of the electric force rather than by using high gas pressures with the consequent need of high electric forces. When a large positive charge was received by the electrode A a negative charge could not be detected on C until Z reached a value of about 25 V./cm. and Z/p a value of 50, and further the magnitude of any negative charge collected by C was always proportional to the magnitude of the positive charge received by A. Hence the electrons collected by C were produced as a result of the action of the positive ions on A. This point was further tested with an apparatus[3] in which the part of the electrode A on which the positive ions fall could be removed by a magnetically operated slider. The positive ions could then pass through the opening and be collected on another electrode. Within the range of Z/p used the negative charge collected by C was always proportional to the positive charge received by A.

As the electrons which are set free from the cathode A move through the gas towards the electrode C they produce more electrons by ionization by collision. Hence the negative charge n received by C in any interval of time is greater than the negative charge n_0 liberated at A by the positive ions during that interval. The relation between these charges is given by the well-known Townsend equation

$$n = n_0 \epsilon^{\alpha x} / \{1 - \gamma (\epsilon^{\alpha x} - 1)\} \qquad \ldots\ldots(1),$$

where $x = d - \delta$, δ being a certain minimum distance before ionization commences and d the distance between the parallel electrodes A and C, while α is the coefficient of ionization by electrons. We are not here concerned with the exact process of ionization represented by the coefficient α; it is sufficient to know that values of α have been determined experimentally for the case in which the above relation represents the growth of photoelectric currents between parallel plates under conditions similar to those discussed here. The presence of the magnetic field modifies to some extent the values of α obtained when the magnetic field is absent owing to the increased distances traversed by the electrons, but this modification is so small that it can be ignored here.

If q is the total positive charge received by A in the given time interval, then, remembering that

$$n_0/(q - n) = \gamma,$$

we find that

$$\gamma = n/(q\epsilon^{\alpha x} - n) \qquad \ldots\ldots(2).$$

The values of γ* found from this relation by measuring n and q at various values of Z/p in a number of experiments are shown in figure 2.

* *Footnote added August* 8, 1936. We are very much indebted to Dr S. P. McCallum for providing us with recently checked values of the coefficients α and γ in pure argon for various values of Z/p, obtained by measuring the growth of currents, and for giving us access to the MSS. of unpublished papers. These values of α have now been used with equation (2) in order to calculate the values of γ given in figure 2. If the earlier determinations of α are used γ works out at about 15 per cent lower. See, for instance, Ayres, *Phil. Mag.* **45**, 353 (1933).

Now in deriving the above expression for γ it is assumed that all the electrons liberated from the cathode A finally arrive at C. However, in general, this does not occur, because the electrons in the space AB diffuse in all directions, and further the process of diffusion is very marked in argon. Those electrons which diffuse back to the cathode are recaptured there, and so are removed from the current. Hence it is necessary to investigate this process more fully before the values of γ given in the curve can be considered to represent the actual number of electrons liberated at the cathode per positive ion. In the above expressions it merely represents the number of electrons which actually move away from the cathode and contribute to the current.

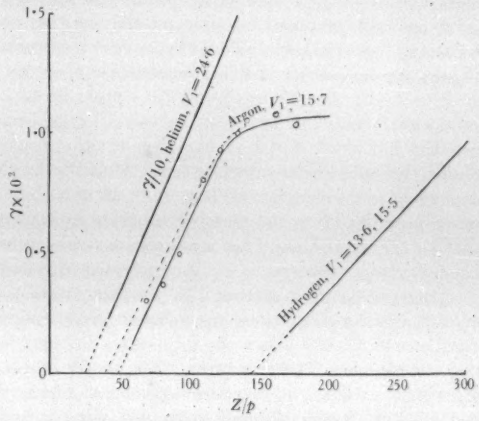

Figure 2. Results obtained with copper cathode.

Now the scattering of photoelectrons back to the cathode from which they were emitted has been investigated theoretically by Young and Bradbury[6], who expressed the ratio of the actual photoelectric current i to the saturation value i_0 of the current in terms of the ratio Z/p. They found that i, i_0

$$i/i_0 = f(a), \qquad a$$

where

$$a^2 = LZ/E_0 p.$$

Values of the ratio i/i_0 corresponding to various values of the expression $f(a)$ are given in their paper.

L is the mean free path of the electrons in the gas at a pressure of 1 mm. and E_0 is the energy, in electron-volts, with which they are emitted from the cathode. In determining this function it was assumed that the return of an electron to the cathode was determined by the first collision with a gas atom after emission. Let us apply this relation between i/i_0 and a to the results given in figure 2 in order to determine how far the currents were from saturation. We must first estimate the L E_0

value of E_0. From the experiments of Oliphant[3,7] it is known that although there are some electrons with energies $V_1 - \phi$, where V_1 is the potential energy of the ion and ϕ the work function of the cathode, most of the electrons have energies of only one or two volts. Thus assume E_0 to be 1·5 volts and let L be taken as 1 mm. approximately[8]; then when $Z/p = 150$, $a^2 = 7{\cdot}5$ and $i/i_0 = 0{\cdot}85$, and for the lower limit $Z/p = 50$, $a^2 = 2{\cdot}5$ and $i/i_0 = 0{\cdot}75$. From this it is seen that correction for the backward scattering of the electrons results approximately in the displacement of the curve to the left into the position shown by the dotted line.

V_1
ϕ

§ 5. THE DISCUSSION OF THE RESULTS

The secondary emission produced by argon positive ions has been measured previously by Penning[9], who obtained values of γ for ions of energies of the order of 80 volts striking a degased cathode of nickel *in vacuo* ($\phi = 5$ V.). By extrapolating the {γ, energy} curve to zero energy it was found that a probable value of γ for ions of very low energy was 0·005. It is seen that this value is in agreement, as far as order of magnitude is concerned, with the values given in the curve, figure 2. Now on the assumption that even under intense electric fields the ionizing action of positive ions is confined to the liberation of electrons at the cathode, it is possible to calculate values of γ on the Townsend theory of sparking by equating the denominator in equation (1) to zero. However, it is not easy to obtain accurate results in this way owing to the large variations in sparking potential with distance and the consequent uncertainty in the exact value of Z/p. Further, to find γ at low values of Z/p it is necessary to use high gas pressures and therefore intense electric fields. McCallum and Klatzow[10] found values of γ from 0·004 to 0·005 for argon ions striking a nickel cathode when Z/p lay between about 100 to 250; and a value of 0·018 when Z/p was 40. Again, from the sparking-potential curves of argon given by Penning and Addinck[11] values for γ of 0·005 when $Z/p = 70$ and 0·018 when $Z/p = 20$ are found for an iron cathode; here $\phi = 4{\cdot}7$ V., $Z = 500$ V./cm. and $p = 25$ mm. A more accurate method of estimating γ is to measure the rate of growth of photoelectric currents in the gas. In this way McCallum and Klatzow[10] found γ to be about 0·004–0·005 with values of Z/p between 80 and 175, again with a nickel cathode.

The secondary emission from copper, measured as a function of Z/p, has previously been determined with positive ions of hydrogen[12] and also with positive ions of helium[13], and these results are given for comparison in figure 2. From the shape of the two curves it would appear that extrapolation to low values of Z/p is reasonable, and from this it follows that γ becomes zero in hydrogen when $Z/p < 100$, and in helium when $Z/p = 15$, but correction for the backward diffusion of the electrons would reduce this value. Further, if extrapolation is justifiable here it follows from figure 2 that in argon γ decreases to zero when Z/p is less than about 40. In fact, in these experiments with argon any charge received by the collecting-electrode C during an interval of about 10 sec. could not be measured on the electrometer, when $Z = 20$ V./cm. or $Z/p < 45$. Again in the experiments

with hydrogen ions no secondary emission was detected when $Z/p < 80$. Hence these curves lead to the conclusion that electrons are not emitted from an electrode in a gas by the impact of positive ions when these have energies not very different from that of the gas atoms.

Now there is evidence[7, 9] to indicate that some secondary emission does occur with ions of low energy striking a degased electrode *in vacuo*; but these conditions are not those obtaining in a discharge through a gas. Further, it is well established that the secondary emission is profoundly affected by the state of the surface of the target. However, the present experiments with argon and the earlier ones with hydrogen and helium lend support to the idea that when the cathode is immersed in a gas, as is the case in a gas-discharge tube, and the electric intensity near the cathode is not very great, the escape of secondary electrons does not occur, whereas it could occur without hindrance if the cathode were degased and *in vacuo*.

It is now interesting to consider the nature of the ions employed in the previous experiments with hydrogen. From the experiments of Smyth[14] and of Hogness and Lunn[15] it would appear that the primary product of ionization in the region EB of the apparatus is the ionized molecule H_2^+, but that the atomic ion H^+ is readily produced by the dissociation of the molecular ion in subsequent collisions and that H_3^+ ions may be formed. Further, the work of Kallman and Bredig[16] shows that this atomic ion tends to persist, since they found that the ratio H^+/H_2^+ increased when the pressure of the gas was increased from $0{\cdot}1 . 10^{-2}$ to $1{\cdot}0 . 10^{-2}$ mm. Moreover, it would be difficult for a massive H_3^+ ion to attain high energies owing to collisional losses, and the process of electron-exchange would tend to limit the energy of the H_2^+ ions as they move through the gas, but the effect of this process in limiting the energies of the atomic ions would be much less[17, 18, 19]. Again, the work of Bleakney[20] and Lozier[21] has indicated the presence of high-speed atomic ions in hydrogen produced by electrons with energies of about 30 eV., and such electrons should be plentiful when Z/p is about 300. Hence it is reasonable to suppose that the positive ions which were received by the copper cathode in the experiments with hydrogen contained a large proportion of atomic ions when they had attained high energies under the fields used in those experiments, in which $150 < Z/p < 400$. This view is supported by the fact that copious ionization by the positive ions by collision with the gas molecules was recorded. However, these considerations make it all the more remarkable that the secondary emission due to the hydrogen ion was so small when compared with that due to the argon ions and the very efficient helium ion, because the kinetic energies of the hydrogen ions were certainly very much greater than those of the argon ions at the same values of Z/p. It would seem probable that this difference in efficiency of the various ions is due partly to their different potential energies. Thus on this view the helium ion, for which $V_1 = 24{\cdot}6$ V., would then be more efficient than the hydrogen atomic ion, for which $V_1 = 13{\cdot}5$.

§6. ACKNOWLEDGEMENTS

We wish to thank Dr S. P. McCallum for very helpful conversations and for giving us access to some unpublished results, and to Prof. E. J. Evans for extending the facilities of his laboratory.

NOTE ADDED IN PROOF

In a recent paper, *Physica*, **3** (**6**), 515 (1936), Kruithoff and Penning have estimated γ for argon ions striking copper by measuring the growth of photoelectric currents. Values of γ from $8{\cdot}8.10^{-3}$ to $3{\cdot}76.10^{-2}$ were found, but there was no consistent variation with Z/p. However, in one experiment an average value of $1{\cdot}2.10^{-2}$ was obtained, which agrees well with the maximum value $1{\cdot}1.10^{-2}$ found in the present direct experiments.

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WIRELESS WAVES REFLECTED FROM THE IONOSPHERE AT OBLIQUE INCIDENCE

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ABSTRACT. The waves emitted by a pulse transmitter at Cambridge were simultaneously received at a point distant 1 km. and at Edinburgh distant 464 km. in a direction 15° west of magnetic north. The variation of equivalent path with emitted frequency was studied for waves of such a frequency that they nearly penetrated the *F* region. The results agreed qualitatively with a simplified theory, and under certain conditions showed the possibility of two transmission paths to the distant point. A quantitative discrepancy between the simple theory and experiment was noticed and its possible explanations are discussed. It is shown that by comparing the frequencies which just penetrate the *E* region at normal and oblique incidence it might be possible to decide whether the Lorentz polarization term should be included in calculating the force on an electron in the ionosphere. Experiments made for this purpose provided only a statistical result on account of the variable nature of the *E* region. Measurement of the sunrise increase of absorption for waves received at the two points indicated that the day-time absorption takes place in a region below the main deviating portion of the *E* region, for echoes both from the *E* and from the *F* region.

§ 1. INTRODUCTION

Most of the experiments in which wireless waves have been observed after reflexion from the ionosphere have been made with the sender and receiver close together, so that the waves were incident on the ionosphere at small angle of incidence. There have, however, been a few experiments in which reception has taken place simultaneously at nearby and distant receiving stations. Appleton and his collaborators [1,2] and Martyn, Cherry and Green [3] have described experiments of this type in which the Appleton frequency-change technique was used. In these experiments the mean wave-frequency was kept constant and observations were made of the way in which the equivalent reflection height P' changed with the time t; this procedure may be referred to as the $\{P', t\}$ technique. The present paper is an account of similar experiments in which the Breit and Tuve pulse method was used, and in which the wave-frequency f could be varied continuously over a wide range; this procedure may be referred to as the $\{P', f\}$ technique.* Two receivers were employed, distant 1 and 464 km. from the sender. The chief points investigated were (*a*) the behaviour of waves of such frequency that they were just about to penetrate the *F* region (§ 3), (*b*) the behaviour of waves just about to penetrate

P'
t
f

* See note at end of paper.

the *E* region (§ 4), and (*c*) the way in which the absorption depends on angle of incidence (§ 5).

At first sight it might be thought that by comparing the behaviour of waves at normal and oblique incidence it would be possible to investigate the form of the wave-trajectory and the distribution of ionization between the *E* and *F* regions. Martyn[4] has, however, shown that if the earth's magnetic field is neglected it is possible to deduce the behaviour of a wave at oblique incidence from that of a wave of a different ("corresponding") frequency at normal incidence, and that this deduction is independent of any particular distribution of ionization. If, therefore, the equivalent height of the wave is known as a function of frequency for normal incidence, then it can be deduced for oblique incidence. Our experimental results concerning the penetration of the *F* region agree qualitatively with the deductions from Martyn's theorem, but there is a quantitative discrepancy which is discussed below in some detail.

In § 4 it is shown that by comparing the *E*-region penetration frequencies for normal and for oblique incidence it should be possible to decide whether or not the Lorentz polarization term[5] is to be included in calculating the force on an electron in the ionosphere. Experiments made with this object are described, but it is pointed out that, owing to the inconstant nature of the *E* region, the results are only statistical in nature.

Appleton and Ratcliffe[1] have pointed out that by comparing the absorption of waves for different angles of incidence it is possible to decide whether the absorption occurs in a relatively non-deviating region situated below the level of the main deviation, and they made some experiments, using continuous wave emissions, to investigate this point. There are several advantages in using the pulse technique for this kind of measurement since it enables observations to be made on individual echoes instead of only on the resultant down-coming wave. Experiments of this kind are described in § 5.

§ 2. EXPERIMENTAL ARRANGEMENTS

A pulse-transmitter similar to that described by Ratcliffe and White[6] was situated at Cambridge, and was provided with a series of coils and aerials so that it would cover the frequency range from 6·0 to 0·67 Mc./sec. The aerials were horizontal wires approximating to half-wave aerials for the mean wave-length of each coil. The emitted waves were received simultaneously at a hut in Cambridge distant 1 km., and at Edinburgh distant 464 km. from Cambridge in a direction 15° west of magnetic north.

The tuning-condenser at the transmitter could be varied by means of a distant control from the Cambridge receiving-hut, so that the emitted frequency could be changed continuously over the whole range of one coil. The coils and aerials could also be interchanged by means of relays worked from the receiving-hut. The signal at the Cambridge receiver was made to give a stationary pattern of the usual kind on the screen of a cathode-ray oscillograph, the time base being driven by the same a.c. mains as those which drove the transmitter.

The receiver at Edinburgh was situated in the Physics Laboratory of the University, and at this distance the received signal consisted only of the pulses reflected from the ionosphere, the ground wave being too weak to be observed. It was not possible to drive the time base from the a.c. mains as at Cambridge, because the mains at the two places were not exactly synchronized. It was therefore necessary to use a self-synchronizing time base which was driven by the received signal. This apparatus was developed by one of us (F. T. F.) in collaboration with Mr S. H. Falloon and has been described elsewhere[15].

§ 3. PENETRATION OF THE *F* REGION

To investigate the penetration of the *F* region at oblique incidence, $\{P', f\}$ curves, showing equivalent path as a function of frequency, were plotted at the two receiving stations simultaneously. At Cambridge equivalent paths were measured directly, but at Edinburgh, where there was no ground ray, the differences between

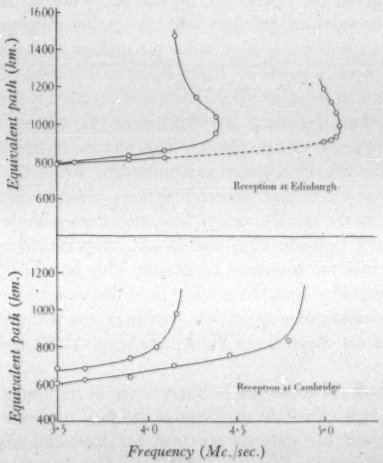

Figure 1. The left-hand curves refer to the ordinary wave, and the right-hand to the extraordinary.

the equivalent paths of the various echoes were measured. As a first approximation it was assumed that the doubly reflected extraordinary wave at Edinburgh was reflected from the same equivalent height as that measured at Cambridge,* and from this the other equivalent heights were calculated. The results of a typical experiment are shown in figure 1. Over the dotted portion of the curve the extraordinary echo alone was present so that it was impossible to estimate the magnitude of the equivalent path, but for those frequencies for which the echo was split the

* The doubly reflected wave has angle of incidence approximating most nearly to the vertical, and the extraordinary wave suffers least group-retardation.

magnitude of the splitting was accurately measured. The dotted portion of the curve has been drawn as a copy of the curve for the ordinary wave.

We turn now to a theoretical discussion of the experimental curve of figure 1. If a $\{P', f\}$ curve is observed at normal incidence, it is possible to deduce the $\{P', f\}$ curve which should be observed at a distant point by making use of a theorem due to Martyn[4], which states that if $P'(f, \theta)$ represents the equivalent path
θ observed for a frequency f and an angle of incidence θ, and if

$$1-\mu^2=AN/f^2 \qquad \text{.....(1),}$$

μ, A, N where μ is the refractive index, A a constant, and N the electron-density,

then $$P'(f\cos\theta, 0)=\cos\theta . P'(f, \theta) \qquad \text{.....(2).}$$

This relation holds whatever the vertical distribution of ionization. If we relate
x the horizontal distance of transmission x to the other quantities by the expression

$$x=P'(f, \theta)\sin\theta \qquad \text{.....(3),}$$

then from the observed $\{P', f\}$ curve at normal incidence we may calculate x as a function of θ for a series of different frequencies, by eliminating $P'(f, \theta)$ from (2) and (3). Figure 2 shows this relation for the ordinary wave, calculated from the normal incidence curve of figure 1. From figure 2 it is next possible to construct curves showing angle of incidence as a function of frequency for a fixed distance of transmission, and then, by using the expression (3), curves of equivalent path as a function of frequency may be plotted. This is done in figure 3 for $x=464$ km., to correspond to the case of reception at Edinburgh. From the curves of figures 2 and 3 it is seen that for certain wave-frequencies it is possible to have two rays joining two points on the earth's surface, one with a steep angle of incidence and a flat-topped trajectory, and the other with a less steep incidence and approaching more nearly to an inverted V-shaped trajectory. This possibility has been pointed out by other investigators, and has usually been discussed by considering a $(\sin)^2$ distribution of ionization-density[7,8]. In virtue of the form of equation (1) our calculation neglects the effect of the earth's magnetic field, and does not include the Lorentz term.

The experimental curve for the ordinary wave is plotted with the theoretical curve in figure 3. It is clear that the form of the two curves is the same but that quantitative agreement can only be obtained by displacing the calculated curve towards the smaller frequencies by 0·23 Mc./sec. Four curves of the type shown in figure 3 were obtained on two separate nights, and they all show the same frequency-displacement. In order to plot curves of this type it is essential that the F-region echo should be sharply defined, and on several nights the experiments were useless because this was not the case.

The quantitative discrepancy may arise from the neglect of one or more of the following factors: (*a*) presence of the earth's magnetic field, (*b*) the possible necessity for including the Lorentz term, (*c*) variation of ionization-density with latitude, and (*d*) curvature of the earth.

It is well known that at normal incidence the critical electron-density required to reflect the ordinary wave is independent of the earth's magnetic field, but at

oblique incidence this is not necessarily the case. The detailed application of Appleton's magneto-ionic theory to the case of oblique incidence on the ionosphere is complicated owing to the varying angle between the direction of propagation and

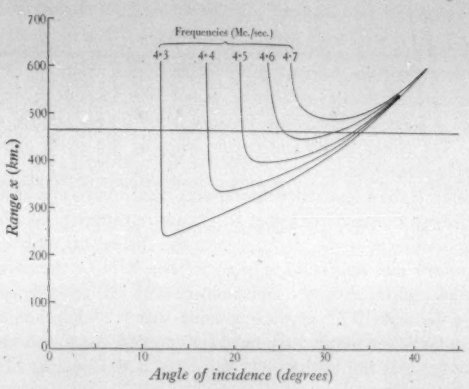

Figure 2.

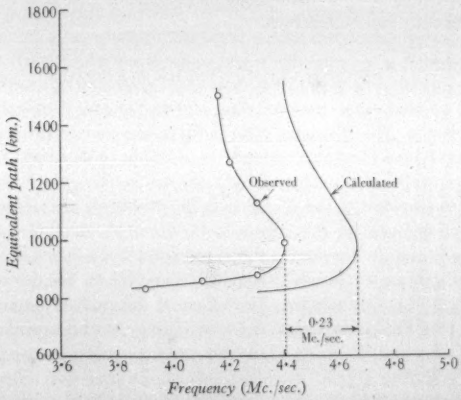

Figure 3.

the direction of the magnetic field, and a full solution has only recently been attempted by Booker[9], who is now trying to adapt his analysis to our special case. We cannot tell yet, therefore, whether the discrepancy is to be explained in this way.

That the inclusion of the Lorentz term also produces a correction which is dependent on the angle of incidence θ is easily seen by considering reflection from

a slab of uniform ionization-density not subject to a magnetic field. The ratio of the penetration frequency for oblique incidence to that for normal incidence is then

$$\sqrt{\frac{\sec^2\theta - l}{1 - l}},$$

l where l has the value 0 or $\frac{1}{3}$ according as the Lorentz term is excluded or included. The effect of including the Lorentz term for reflection from the *F* region, with its gradual variation of ionization-density, is not easy to deduce, mainly because when this term is included the group-velocity is no longer simply related to the phase-velocity. We cannot at present decide whether the effect of including this term would explain our results.

An explanation of the quantitative discrepancy on the basis of a latitude variation of ionization-density would require that the ionization-density should decrease as we go north on a summer night. Reference to the theoretical ionization curves of Millington[10] shows that we should expect the reverse to be the case, but in view of the fact that at a given point the ionization-density has recently been shown to increase during the night[14], it appears possible that it should actually be less in the north where night conditions have not been in existence for so long.

We are satisfied that the curvature of the earth is not responsible for the discrepancy revealed by figure 3.

Further experimental and theoretical investigations are required before the quantitative difficulty can be resolved.

§ 4. PENETRATION OF THE *E* REGION

It has been pointed out in the preceding section that, for a sharply defined slab of uniform ionization, the calculated ratio between the penetration frequencies for normal and for oblique incidence depends on whether or not the Lorentz term is included. Since curves of equivalent height against frequency at normal incidence show that the lower edge of the *E* region is fairly sharply defined, we may, to a first approximation, consider this region to be a sharply defined slab of uniform ionization-density and, by comparing the penetration frequencies of this region for normal and for oblique incidence, it should be possible to decide whether or not the Lorentz term is to be included. The effect of the earth's magnetic field may be eliminated to a first approximation by observing on the ordinary wave only, since for this, assuming the quasi-transverse approximation to the magneto-ionic theory in the reflecting region, the ionic density required for reflection is independent of an external field.

A series of experiments was made to determine the penetration frequencies of the *E* region for reception at Cambridge and at Edinburgh. Difficulty was experienced in estimating the critical frequency as observed at the distant station owing to the fact that partial reflection often occurred for frequencies higher than the true penetration frequency. For normal incidence this difficulty was not serious, since the appearance of an *F* echo could be taken to represent the penetration of the *E* region, even if it was accompanied by an echo partially reflected from the

E region. At oblique incidence, however, this criterion could not be used, since *E* and *F* echoes were present together over a wide frequency-range. It is explained in the next section that this is because the *F*-region echo penetrates the *E* region on account of its steeper angle of incidence. We took that frequency at which the amplitude of the *E* echo fell considerably below that of the *F* echo as giving an upper limit for the penetration frequency.

It was found on some nights that the conditions in the *E* region were not steady, and observations could not be repeated, while on other nights there was so much partial reflection that no precise estimate of the penetration frequency could be made. Out of fourteen nights' experimenting only five were found to yield reliable results. The results obtained on these nights give rise to the values for l shown in table 1.

Table 1. Experimental values of l

Date May 1935	Values deduced for l
8	0·16, 0, −0·3, −0·3
13	0·06, 0·29, −0·3
14	0·03, −0·7
20	0·5, −0·2, 0·07, 0·26
21	−0·7, 0·05

The mean of these values is 0·05, but in view of the large spread in the readings themselves it is doubtful whether this set of results can decide between the possible values 0 and $\frac{1}{3}$. In considering these results it is further to be remembered that we have assumed that the ionization-density does not vary with latitude.

The penetration frequencies observed at the two points often showed rapid changes which were quite unrelated to each other, indicating that the ionization-densities above Cambridge and above the mid-point between Cambridge and Edinburgh were varying in an unrelated manner. This type of behaviour suggests that the *E* region is not uniformly ionized in a horizontal direction. If we picture the *E* region as composed of clouds of more and less dense ionization we can explain these results as well as the results of Ratcliffe and Pawsey[11] on the lateral deviation of reflected waves, and we have a simple mechanism for the partial reflection and partial transmission which is so frequently observed at vertical incidence, without the necessity of assuming an extremely sharp boundary for the layer.

The fact that the electron-density in the *E* region could sometimes be greater near the mid-point than at the ends of the transmission path was apparent from the frequent occurrence of echoes with an equivalent path corresponding to the type of trajectory shown in figure 4. This type of echo occurred much more frequently for the oblique than for the normal transmission.

Figure 4.

We conclude therefore that without experimental knowledge of the variations in ionization-density over the mid-point of the trajectory, and in the absence of a

very large number of observations, this type of experiment cannot give a reliable result concerning the Lorentz term.

§ 5. ABSORPTION

Information about the absorption of waves may be obtained by comparing the amplitudes of echoes returned at oblique and at normal incidence. Appleton and Ratcliffe[1] have discussed the way in which the absorption of waves varies with angle of incidence in the two cases (i) where the absorption occurs near the top of the trajectory and (ii) where the absorption occurs in a relatively non-deviating region below the main deviating region. They point out that for case (i) the absorption decreases as the angle of incidence increases,* whereas for case (ii) the absorption increases as the angle of incidence increases.

In considering case (i) they discussed two special types of ionization-gradient and their conclusions have since been verified for other ionization-gradients by Martyn[4] and by Norton, Kirby and Lester[12]. In attempting to decide whether case (i) or case (ii) represents the facts the more correctly, the above-mentioned workers have attempted to measure the amplitude of the down-coming wave for different angles of incidence, but in interpreting the experimental results it has been necessary to make assumptions about the vertical polar diagram of the sending aerial.

In the present series of experiments observations of the amplitudes of the waves reflected from the *E* region were made at normal and at oblique incidence during the sunrise period. The height of the *E* region remained very constant during the period of observation, so that the angle of incidence was constant. By confining attention to the *increase* of absorption at sunrise, results were obtained which were independent of the angular distribution of radiation at the transmitter. The amplitudes of the echoes were measured by means of the length of the trace which they formed on the oscillograph screen, the sensitivity of the apparatus being altered from time to time by means of a calibrated gain-control. This rough measurement was sufficient for the purpose, indeed it would have been difficult to devise a more accurate method on account of the pronounced fading which occurred with all echoes.

Measurements of this kind were made on four separate occasions, viz. 4, 6, 7 and 14 May 1935, the wave-frequency being 1·67 Mc./sec. (wave-length 180 m.). It was found that the effect of absorption was first evident at the distant station about half an hour before ground sunrise, and that one hour after sunrise the amplitude had fallen to about 0·06 of the night-time value. For normal incidence the effects of absorption were not noticed until about one hour after sunrise, and then the amplitude had fallen to about half its night-time value. Three and a half hours after sunrise the amplitude measured at normal incidence was reduced to

* There is a misprint in the middle of page 155 in their paper where it is stated that "the *reflection* coefficient is less for the more distant stations"; this should obviously read "the *absorption* coefficient is less for the more distant stations" in agreement with the equations at the top of the previous page.

0·25 of the night value, whereas the signal was quite unobservable at oblique incidence.

The fact that waves arriving at oblique incidence are strongly absorbed near sunrise, whereas those arriving at normal incidence are absorbed much less, is apparent when one is watching the echoes from a nearby pulse transmitter, for it is very noticeable that the background mush disappears during the half-hour after sunrise, whereas at these frequencies the echo signal does not alter appreciably.

From these results it is quite clear that the day-time absorption at oblique incidence is much greater than that at normal incidence, so that the second assumption of Appleton and Ratcliffe appears to be true, and the absorption occurs in a relatively non-deviating region below the main deviating region. It is interesting to see whether this assumption leads to the observed numerical relation between the absorption at vertical incidence and that at oblique incidence. To calculate the absorption at oblique incidence we consider the up-going and the down-coming paths separately, and we assume that the direction of transmission through the absorbing region is that corresponding to a sharp reflection at a height of 100 km. The value of the absorption coefficient in a region where the refractive index is approximately unity has been given in a previous paper[13], and has been shown to be inversely proportional to either

$$(a)\quad (f+f_H\cos\theta')^2$$

or

$$(b)\quad (f+f_H\cos\theta'),$$

according as one or other of two assumptions is made. Here f_H is the magneto-ionic gyro-frequency and θ' is the angle between the ray and the earth's magnetic field. f_H

We here restrict our calculations to the ordinary wave, since for the frequencies we are considering the amplitude of the extraordinary wave is negligible in comparison. In the particular case considered here it happens that the up-going wave travels exactly at right angles to the earth's magnetic field, so that the quasi-transverse approximation to the magneto-ionic equations should be used. Although the expressions given above are deduced for the quasi-longitudinal case they reduce to the quasi-transverse case when θ' is put equal to $\pi/2$ so that we may use them as they stand. For a slab of absorbing region the ratio of the integrated absorption coefficients for the vertical and the oblique paths is given by

$$\sec i_0 \left\{\frac{1}{(f+f_H\cos\theta'_1)^2}+\frac{1}{(f+f_H\cos\theta'_2)^2}\right\} \div \left\{\frac{2}{(f+f_H\cos\theta'_0)^2}\right\}$$

in case (*a*) and by a corresponding expression in case (*b*), where i_0 is the angle of incidence, and θ'_0, θ'_1, θ'_2 are the angles which the ray makes with the earth's magnetic field in the case of the vertical ray, the up-going oblique ray, and the down-coming oblique ray respectively. i_0 $\theta'_0, \theta'_1, \theta'_2$

Calculating in this manner we find the following results for the ratio of the integrated absorption coefficients:

5·45 for assumption (*a*),
3·62 for assumption (*b*).

The observations already mentioned indicate that one hour after sunrise the ratio of the integrated absorption coefficients was

$$\frac{\log 0{\cdot}06}{\log 0{\cdot}5}\text{, which} = 4{\cdot}0.$$

To the order of accuracy of the experiment this may be considered as being in agreement with either of the assumptions.

These results indicate that the absorption which becomes apparent after sunrise occurs in a relatively non-deviating region below the *E* region, and this conclusion is in agreement with the deductions made by Appleton and Ratcliffe[1], who observed near sunset, and by Farmer and Ratcliffe[13], who observed near the middle of the day. They do not agree with those of Martyn[4] whose observations lead to the conclusion that the absorption is in the topmost portion of the wave-trajectory, but it must be remembered that his conclusions were based on night-time observations.

When observing at oblique incidence it is possible to receive echoes simultaneously from the *E* region and from the *F* region, the wave from the *F* region having penetrated the *E* region because of its steeper angle of incidence. By using these two waves it is possible to investigate simultaneously the absorption suffered by each separately; this can never be done at vertical incidence, since the two reflections do not occur together.* Observations at Edinburgh, made with a wavelength of 180 m. on the *E* and *F* echoes, which were visible simultaneously during the sunrise period, indicated that the amplitudes decreased together, the amplitude of the *F* echo decreasing slightly more than that of the *E* echo. This seems to indicate that the absorption takes place in the same region for both echoes, and that there is no pronounced absorption of the *E* echo near the top point of its wave-trajectory. The slight extra absorption of the *F* echo may be due to its having traversed the upper portion of the *E* region.

§ 6. ACKNOWLEDGEMENTS

We are much indebted to Prof. Barkla for providing us with very suitable accommodation in his laboratory at Edinburgh, and for making us so comfortable during our stay there. We also wish to acknowledge the help which we have received from the Department of Scientific and Industrial Research, who have made a grant to one of us (F. T. F.) and who have lent us some of the apparatus. We are further indebted to Mr H. G. Booker for many helpful discussions on theoretical points.

NOTE ADDED IN PROOF

After this paper had been communicated an account of similar work was published in Germany, *Hochfrequenztech. u. Elektroakust.* **48**, 1 (1936), by Crone, Kruger, Goubou and Zenneck. They used the Breit and Tuve pulse technique and the $\{P', t\}$ method of observing, and compared reception at normal and at oblique incidence. The main phenomena recorded in their paper agree with those which we found by means of the $\{P', f\}$ technique.

* Except under conditions of partial reflection, which are not suitable for the present purpose.

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THE ELECTRICAL CONDUCTIVITY OF BARIUM CHLORIDE AND ITS VARIATION WITH TEMPERATURE

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ABSTRACT. The electrolytic conductances of aqueous solutions of barium chloride have been measured over a wide range of concentration and temperature. The equivalent conductivities at infinite dilution have been found by the method of Shedlovsky, and a formula connecting conductivity and temperature is given.

§ 1. INTRODUCTION

Beyond the recognition of the fact that electrolytic conductivity varies extremely rapidly with temperature, the problem of the temperature variation has received very little attention, in marked contrast with the large amount of work that has been done on the variation with concentration.

Kohlrausch[1] studied the variation of a number of strong electrolytes in water over the restricted range of temperature 0–30° C., whilst, on the other hand, Noyes[2] has carried out measurements over a much wider range extending to 306° C., but in no great detail.

Recently Welton[3] investigated the electrical conductivity of aqueous solutions of potassium and sodium chlorides over a temperature range 18–85° C. Following this path, Clews[4] studied aqueous solutions of potassium nitrate, sodium sulphate and potassium sulphate over the same temperature range. The present paper, forming an addition to this series, deals with a bi-univalent salt, namely barium chloride. This salt was selected because of its convenient chemical properties; the crystals can be dehydrated by heat without any formation of hydrochloric acid, and the salt is not appreciably hydrolysed even in hot aqueous solution.

§ 2. EXPERIMENTAL METHOD

The Wheatstone network employed was that described by Clews[4]; it consisted of a ratio box, a six-dial decade resistance box, and the conductivity cell. All the resistances used were of low inductance, and a very sharp balance point was obtained by the inclusion of a variable condenser in parallel with the measuring resistance. By means of a mercury rocking key the positions of the cell and the measuring resistance could be reversed with respect to the ratio arms.

A one-valve oscillator of the tuned-anode type was again used as source of current, and this possessed a frequency of 1152 c./sec., within the range of maximum

sensitiveness of the ear. As before, a telephone receiver connected to the bridge through a two-stage amplifier was used as detector.

The stronger solutions were made up by weight, but below 0·01 *N* the solutions were prepared by dilution. This was done by weighing out a certain volume of 0·01-*N* solution, syphoning conductivity water from a Hartley still into it, and re-weighing. The densities of the 0·01-*N* solution and of the water at 25° C. being known, the respective volumes could be calculated accurately and hence the concentration of the new solution could be determined. By this means contamination of the solution due to long exposure to the air in the laboratory was avoided.

Washburn cells made in pyrex glass were used, the cell constants being determined by means of the 0·1-*D* and the 0·01-*D* Parker solutions containing respectively 7·47896 and 0·746253 g. of potassium chloride in 1000 g. of water. These solutions were assumed to have the new conductivity values as given by Jones and Bradshaw[5].

The thermostat consisted of a well-lagged container filled with liquid paraffin, and this could be rapidly heated by means of a 1200-watt Heatrae heater. To maintain any temperature two Ediswan lamps, each having a carrying capacity of 1 A., were employed, the current through them being operated by means of a Lowry spiral regulator filled with aniline. A rheostat in series with the lamps made it possible to adjust the heating-current to any desired value. With this arrangement the temperature was kept constant to within 0·01° C. over the whole range of temperature. The temperature was measured by means of a mercury-in-glass thermometer, recently calibrated at the National Physical Laboratory, which could be read to within 0·01° C. with the aid of a small microscope.

§ 3. RESULTS

It will be observed that the concentration range covered is from 0·01 to 0·001-*N*. As the temperature rises the concentration of the electrolyte between the electrodes decreases owing to the expansion of the solvent, and this fact must be taken into account when the equivalent conductances are calculated. The results are shown graphically in figure 1. For any given concentration the conductance increases with the temperature, the {conductivity, temperature} curves being slightly concave towards the axis of conductance.

It becomes of interest to see how far the Debye-Hückel-Onsager theory can account for the observed results. For a uni-bivalent electrolyte the Onsager equation assumes the form

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C},$$

in which $$\alpha = \frac{0{\cdot}986 \cdot 10^6 \, 4q\sqrt{3}}{(DT)^{\frac{3}{2}}(1+\sqrt{q})} \quad \text{and} \quad \beta = \frac{29{\cdot}0 \times 3\sqrt{3}}{(DT)^{\frac{1}{2}}\eta},$$

q being given by $$q = \frac{2\Lambda_0}{3(\Lambda_0 + l)}.$$

In this equation D is the dielectric constant, T the absolute temperature, η the viscosity of the solvent, Λ the equivalent conductivity, Λ_0 the equivalent con-

ductivity at infinite dilution, l the mobility of the univalent ion, and C the concentration of the solution.

According to the theory, therefore, a plot of Λ against $C^{\frac{1}{2}}$ should yield at the greatest dilutions a straight line whose slope should approximate to the value given by $(\alpha\Lambda_0+\beta)$.

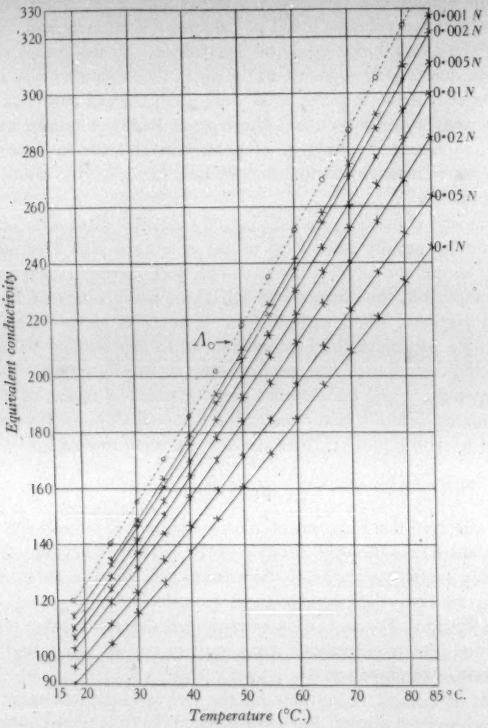

Figure 1.

Figures 2 and 3 show the plots of Λ against $C^{\frac{1}{2}}$ for the present results. The curves do approach linearity as the concentration decreases and can therefore be extrapolated to give approximate values of Λ_0.

By employing Wyman's formula[6] for the variation of the dielectric constant of water with temperature, and consulting the *International Critical Tables* for the {viscosity, temperature} variation, the value of β can be evaluated over the whole range 18–85° C. The calculation of the values of α over the same range

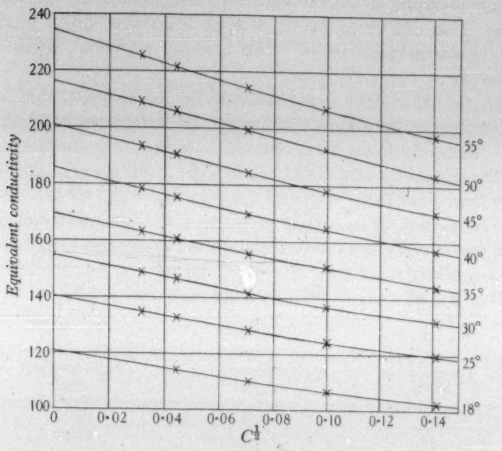

Figure 2.

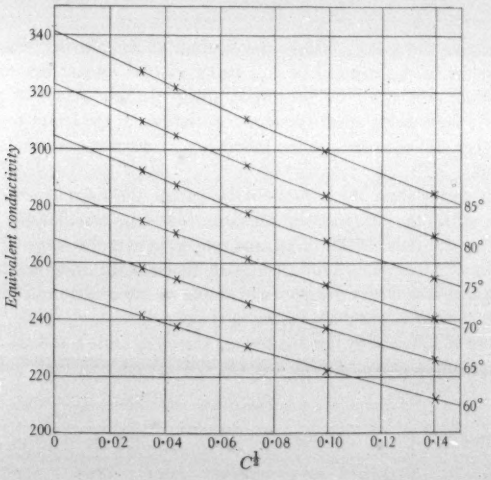

Figure 3.

involves the knowledge of the variation with temperature of the mobility of the chlorine ion. This can be found by plotting the values given in the Landolt-Börnstein physico-chemical tables[7] and drawing a smooth curve through the points obtained.

Although the values thus found can only be approximate, this fact does not seriously detract from the accuracy of the test, since the term in which they occur, namely q, is insensitive to small variations in l. In fact, over the temperature range 18–85° C. the values of q only varied between the limits 0·4321 and 0·4384.

In table 1 some calculated values for the slope of the $\Lambda - C^{\frac{1}{2}}$ curve are compared with the experimental values. While they are of the same order of magnitude it will be seen that in every case the experimental values are less than those calculated, so that Onsager's equation can only apply strictly at concentrations less than 0·001 N. That it does apply within this range, however, appears to be evident.

Table 1

Temperature (°C.)	Theoretical slope	Experimental slope
18	151·8	151·4
25	179·9	168·6
35	224·1	211·1
45	272·0	235·7
55	323·2	284·3
65	380·2	328·6
75	441·0	409·0

To determine the true Λ_0 values the method of Shedlovsky[8] was used, the calculated values of Λ_0, denoted by Λ_0', being plotted against the concentration. For bi-univalent salts at 25° C. Shedlovsky found that the resultant plot was not quite linear[9], there being small systematic deviations at the lower concentrations, which, however, did not preclude the possibility of accurate extrapolation to zero concentration.

Figures 4 and 5 show the curves obtained from the present series of results. From 25 to 35° C. the curves retain the form found by Shedlovsky. Above this range, however, the plots become linear, and remain so over the range of temperature 40–85° C. At 18° C. deviations similar to those found at the other low temperatures exist, but in this case it was thought inadvisable to extrapolate to infinite dilution owing to the somewhat uncertain nature of the curve.

The values of Λ_0 found by this method are shown in table 2 and are not seriously different from those obtained from the $\{\Lambda, C^{\frac{1}{2}}\}$ curves. In fact, substitution of

Table 2

Temperature (°C.)	18	25	30	35	40	45	50
Λ_0	(119·9)	140·1	155·0	170·1	185·6	201·7	218·0
Temperature (°C.)	55	60	65	70	75	80	85
Λ_0	235·0	252·0	269·5	287·0	305·5	323·9	342·3

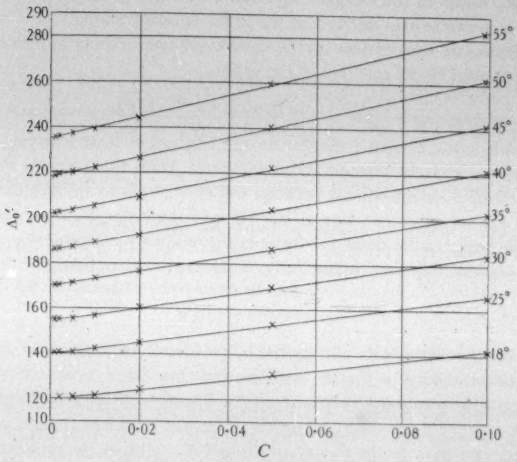

Figure 4.

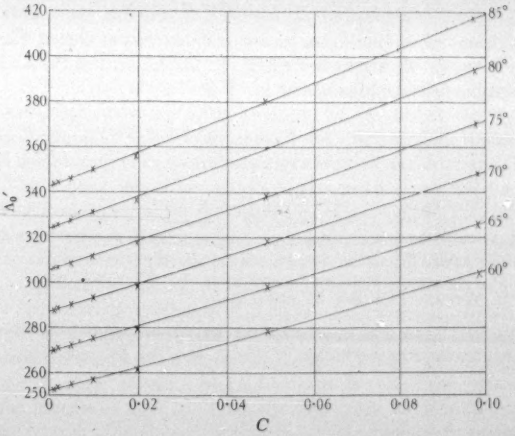

Figure 5.

these new Λ_0 values in the Onsager equation only slightly alters the Λ_0' values at 0·1 and 0·05 N and is inappreciable at the lower concentrations.

The influence of temperature on the equivalent conductivity at infinite dilution can be represented by an equation of the type

$$\Lambda_0{}^t = \Lambda_0{}^{25}\,[1 + a\,(t-25) + b\,(t-25)^2].$$

The constants a and b were evaluated by the method of least squares, the values found being respectively 0·02099 and 0·00005167. With these values for the constants the mean error introduced between the observed and the calculated values of $\Lambda_0{}^t$ over the temperature range 30–85° C. is of the order 0·06 per cent, so that for this wide temperature range the formula forms a very convenient and accurate method of representing the {conductivity, temperature} variation.

§ 4. CONCLUSION

The present investigation affords further evidence in support of the Debye-Hückel-Onsager theory in that it confirms the theoretical predictions as to the behaviour of dilute aqueous solutions of the bi-univalent electrolyte considered, over a wide range of temperature. Further, it becomes evident from this work that an empirical extension of the theory previously thought to be applicable only to uni-univalent electrolytes is valid also for a bi-univalent salt at temperatures above those at which conductivity phenomena are usually studied.

§ 5. ACKNOWLEDGEMENTS

This work was carried out in the physical laboratories at Queen Mary College, and I wish to tender my thanks to Prof. H. R. Robinson, F.R.S., for his interest and advice throughout the investigation.

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THE IGNITION OF EXPLOSIVE GASES

By G. MOLE

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ABSTRACT. It is shown that the activation theory of ignition, when expressed mathematically, leads to a differential equation, the general ignition equation, which represents the state of an ignitible mixture. This equation yields solutions which agree closely with the fundamental phenomena of ignition.

§ 1. INTRODUCTION

Attempts to explain the mechanism of the ignition of explosive gaseous mixtures have proceeded along three lines. Taylor-Jones, Morgan and Wheeler[1,2,3,4] inclined to the view that ignition was a purely thermal process. They supposed that "the ignition of a gaseous mixture depends primarily ...on the heating of a sufficient volume to a sufficient temperature", from which followed as a natural corollary that "the heat energy required in the source for ignition is least when the heat is imparted instantaneously". On the other hand Thornton[5,6], to whom we owe the first proof of the significance of what he termed "the least igniting current", suggested that the role of the igniting source was to produce ions, the interaction of which led to ignition and subsequent flame-propagation maintained by ionization produced by the further chemical reaction. Finch and Thompson[10], however, showed by spectrographic means that the ignition and combustion of explosive mixtures of carbon monoxide and air were not conditioned by a prior ionization of any of the constituents, and they also demonstrated the inadequacy of the thermal theory to account for the facts when they showed that a decrease in discharge-frequency could completely outweigh the effect upon igniting power of a reduction in (i) the total energy, (ii) the rate of dissipation of energy or (iii) both, in ignition by either the first half-oscillation of a condensed discharge or by the whole discharge[13].

The results of further experiments by Bradford, Finch and Prior[14,15] in which explosive mixtures were ignited by coil discharges, showed that the capacity component of the discharge played a part subordinate to that of the inductance component in the process of ignition. They also found that the igniting power of the coil discharge was not a function of the total inductance-component energy alone but was also determined partly by the peak, and partly by the mean rate of dissipation to an extent which varied greatly with the nature of the gas mixture. Finally, they showed that, on thermodynamic grounds, the thermal theory was untenable because

it implied the view that heat was the only form of energy which could produce ignition, and that any other form of energy must be converted into heat before becoming effective[15]. Such a view is in direct conflict with the well-known phenomena of the photo-ignition of hydrogen-chlorine mixtures and the discovery by Dixon and Croft[7] that dilution with oxygen in excess of the equivalent amount reduces the temperature of ignition of hydrogen-oxygen mixtures.

Finch and his collaborators[9, 10, 11, 12, 13, 16, 17] have put forward the view that ignition and self-propellant combustion are determined by the building up of a sufficient concentration of suitably excited molecules. The igniting energy is regarded as the source of suitable excitation in the case of ignition, and the energy set free as a result of the chemical action between excited molecules as the source of supply of the excited molecules which maintain the subsequent independent combustion. This view is now generally known as the *activation theory of ignition*. It has so far been expressed only in qualitative form, i.e. "ignition is primarily determined by the setting up of a sufficient concentration of suitably activated molecules"[13].

There are striking similarities between the behaviour of activated molecules taking part in ignition and gaseous ions undergoing recombination. Thus it would seem that the method successfully applied by Langevin[20] to the quantitative analysis of the phenomena of the recombination of ions might well be adapted to a quantitative study of the mechanism of ignition. This has been attempted in what follows.

§ 2. GENERAL IGNITION EQUATION

t, n, n' Consider the element of gaseous mixture which is the locus of ignition. Let the numbers of suitably activated molecules per unit volume at any time t be n and n'. Let the rates of formation of suitably activated molecules per unit volume at time t be q and q'. Let the rate of combination per unit volume at time t be p and the rates of deactivation per unit volume s and s'. Then, if α is the coefficient of combination,

q, q', p
s, s', α

$$p = \alpha n n' \qquad \text{.....(1).}$$

The general equations of state are

$$\left.\begin{aligned} \frac{dn}{dt} &= q - p - s \\ \text{and} \quad \frac{dn'}{dt} &= q' - p - s' \end{aligned}\right\} \qquad \text{.....(2).}$$

m_1, m_1'
m_2, m_2'
R
j

Let the rates of activation be m_1 and m_1' per unit of energy dissipated by the igniting agent and m_2 and m_2' per unit of energy liberated on combination. Suppose further that the rate of energy-dissipation by the igniting agent at time t is R and that the energy liberated as the result of one combination is j. Then,

$$\left.\begin{aligned} q &= m_1 R + m_2 jp \\ \text{and} \quad q' &= m_1' R + m_2' jp \end{aligned}\right\} \qquad \text{.....(3).}$$

Eliminating q and q' from equations (2) and (3) we have

$$\left.\begin{aligned}\frac{dn}{dt} &= m_1 R + (m_2 j - 1)\, p - s \\ \text{and} \quad \frac{dn'}{dt} &= m_1' R + (m_2' j - 1)\, p - s'\end{aligned}\right\},$$

which may be written

$$\left.\begin{aligned}\frac{dn}{dt} &= m_1 R + \alpha (m_2 j - 1)\, nn' - n/\omega \\ \text{and} \quad \frac{dn'}{dt} &= m_1' R + \alpha (m_2' j - 1)\, nn' - n'/\omega'\end{aligned}\right\} \quad \text{.....(4),}$$

where ω and ω' are the average lives of activated molecules which do not combine. ω, ω'

The supply of explosive mixture may be regarded in practice as inexhaustible. Thus m_1, m_2, ω and j are constant with respect to time. Let the igniting agent be such that R is also constant with respect to time. Equation (4) may then be written:

$$\left.\begin{aligned}\frac{dn}{dt} &= a + bnn' - cn \\ \text{and} \quad \frac{dn'}{dt} &= a' + b'nn' - c'n'\end{aligned}\right\} \quad \text{.....(5),}$$

where a, b, c and a', b', c' are positive constants the values of which are given by a, b, c, a', b', c'

$$\begin{aligned} a &= m_1 R, & a' &= m_1' R, \\ b &= \alpha (m_2 j - 1), & b' &= \alpha (m_2' j - 1), \\ c &= 1/\omega, & c' &= 1/\omega'. \end{aligned}$$

These are simultaneous non-linear differential equations which are easily solved when $n = n'$. Thus,

$$\frac{dn}{dt} = a + bn^2 - cn \quad \text{.....(6).}$$

The solutions are the following.

Case I. $a = 0$.

The complete solution is

$$n = c/b \{1 + (c/bn_0 - 1)\, e^{ct}\} \quad \text{.....(7),}$$

where n_0 is the value of n when $t = 0$. The curve to equation (7) is drawn in figure 1. n_0

Case II. $a < c^2/4b$.

The complete solution is

$$n = \frac{\phi_1 (n_0 - \phi_2)\, e^{\phi_2 bt} - \phi_2 (n_0 - \phi_1)\, e^{\phi_1 bt}}{(n_0 - \phi_2)\, e^{\phi_2 bt} - (n_0 - \phi_1)\, e^{\phi_1 bt}} \quad \text{.....(8),}$$

where ϕ_1 and ϕ_2 are the roots of the quadratic ϕ_1, ϕ_2

$$bn^2 - cn + a = 0.$$

The curve to equation (8) is given in figure 2.

Case III. $a=c^2/4b$.

The complete solution is

$$\left.\begin{aligned} n&=c/2b-1/\{bt+2/(c-2bn_0)\} \\ \text{or}\quad t&=2/(c-2bn)-2/(c-2bn_0) \end{aligned}\right\} \qquad \text{.....(9).}$$

The curve to equation (9) is given in figure 3.

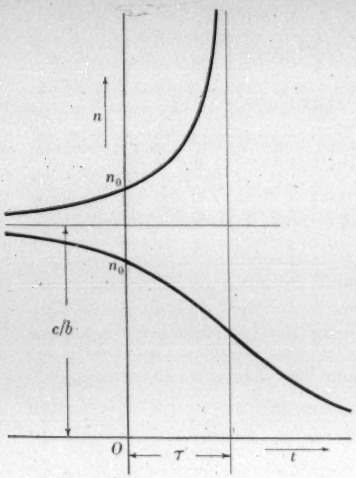

Figure 1. $a=0$. $\tau=\frac{1}{c}\log\frac{bn_0}{bn_0-c}$.

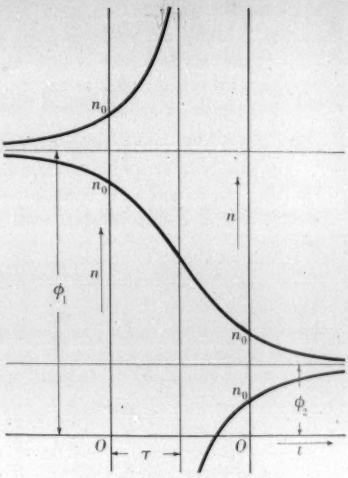

Figure 2. $a<c^2/4b$. $\tau=\frac{1}{b(\phi_1-\phi_2)}\log\frac{n_0-\phi_2}{n_0-\phi_1}$;
$\phi_1=\{c+\sqrt{(c^2-4ab)}\}/2b$; $\phi_2=\{c-\sqrt{(c^2-4ab)}\}/2b$.

Case IV. $a>c^2/4b$.

The complete solution is

$$\left.\begin{aligned} n&=\frac{1}{2b}\left[c+\gamma\tan\left\{\frac{\gamma t}{2}+\tan^{-1}\frac{2bn_0-c}{\gamma}\right\}\right] \\ \text{or}\quad \frac{\gamma t}{2}&=\tan^{-1}\frac{2bn-c}{\gamma}-\tan^{-1}\frac{2bn_0-c}{\gamma} \end{aligned}\right\} \qquad \text{.....(10),}$$

γ where $\gamma=\sqrt{(4ab-c^2)}$.

The curve to equation (10) is given in figure 4.

Thus four distinct types of solution to the general ignition equation are obtainable. The solutions are dependent on the relative values of the quantities a and $c^2/4b$. The condition for self-propagation, $a=0$, leads to the solution of case I (figure 1). From this it is seen that the initial activation n_0 has a critical value c/b below which the concentration of activated molecules n drops to zero as t approaches infinity and above which n proceeds to infinity in the finite time

τ $$\tau=c^{-1}\log\{bn_0/(bn_0-c)\}.$$

This shows that an ignitible mixture, if free from any source of activation, should

remain in stable equilibrium without combustion taking place, but that if it is activated beyond a certain critical value it should explode. This is the most fundamental phenomenon which must be explained by any theory of ignition.

If the intensity of the source of activation is less than the critical value given by $a=c^2/4b$ then the equations of case II (figure 2) apply. Under these conditions it is seen that an explosion will occur only if n_0 possesses a value higher than ϕ_1. The critical value ϕ_1 is however less than the corresponding value c/b for self-propagation. For lower values of n_0 the concentration of activated molecules approaches the steady value ϕ_2 and remains at that value so long as the activating

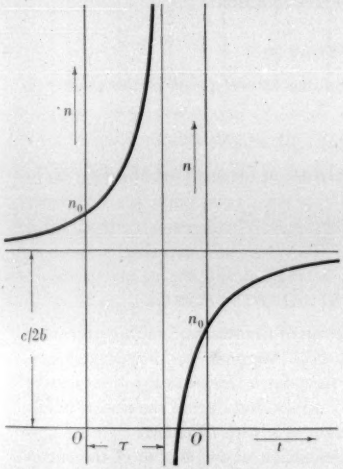

Figure 3. $a=c^2/4b$. $\tau=2/(2bn_0-c)$.

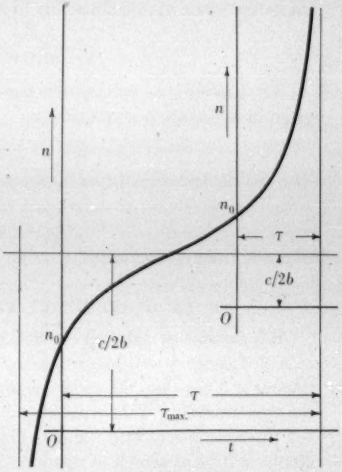

Figure 4. $a>c^2/4b$.

$$\tau=\frac{1}{\gamma}\left(\pi-2\tan^{-1}\frac{2bn_0-c}{\gamma}\right);\ \tau_{\max.}=2\pi/\gamma.$$

source is maintained. Slow combustion is thus to be expected and should occur at a steady rate given by $p=\alpha\phi_2{}^2$. Such slow combustion has often been demonstrated in heated gases, in electric discharges[8, 10, 11, 12, 16] and in mixtures under the influence of photoactive radiation.

When the intensity of the source of activation is greater than the critical value given by $a=c^2/4b$ the equations of case IV (figure 4) apply. Under these conditions the mixture must always explode in the finite time given by

$$\tau=\frac{1}{\gamma}\left(\pi-2\tan^{-1}\frac{2bn_0-c}{\gamma}\right).$$

The time taken to explode can never exceed the value $\tau_{\max.}=2\pi/\gamma$. The critical condition for ignition by a continuous source is thus $a=c^2/4b$. The condition for

$\tau_{\max.}$

ignition by a source of limited duration, obtained by substituting $n_0=0$ and $n=c/b$ in equation (10), is $c=\gamma \tan(\gamma\tau/4)$.

The theory yields one more critical condition. If the coefficient b is negative, i.e. if the value of the quantity $m_2 j$ is less than unity, then the term γ in equation (10) becomes imaginary and equation (7) becomes

$$n=c/b\,\{(1+c/bn_0)\,e^{ct}-1\},$$

from which it will be seen that n approaches zero for all positive values of t. The mixture will therefore neither explode under the influence of an activating agent nor propagate an explosion. It follows that $m_2 j=1$ is the condition which determines the limits of inflammability of an explosive mixture.

§ 3. SLOW COMBUSTION

The rate of slow combustion per unit volume at any point in the mixture is given in molecules per unit time by

$$p=\alpha\phi_2{}^2=\{1-\sqrt{(1-4ab/c^2)}\}^2\,\alpha c^2/4b^2.$$

The rate of slow combustion for the whole mixture or for any part of it is given by

C $$C=\int\frac{\alpha c^2}{4b^2}\{1-\sqrt{(1-4ab/c^2)}\}^2\,dV \qquad \text{.....(11),}$$

V where V refers to volume.

§ 4. IGNITION BY ELECTRICAL DISCHARGE

It is possible to make a theoretical comparison of the relative igniting properties of high-frequency and low-frequency discharges. Suppose the discharge is continuous and possesses the energy-dissipation wave-form shown in figure 5. During the time intervals 1–2 the equations of case IV apply, and during the time intervals 2–1 the equations of case I apply. The variation of n with t for least igniting conditions will be as shown in figure 6. An examination of the shapes of the curves

n_1, n_2 shows that the equilibrium is stable for values of n_1+n_2 less than c/b but unstable for values greater than c/b. The relation $n_1+n_2=c/b$ is therefore the condition for ignition. The following equations are then true:

$$\frac{\gamma\tau}{2}=\tan^{-1}\left(\frac{2bn_2-c}{\gamma}\right)-\tan^{-1}\left(\frac{2bn_1-c}{\gamma}\right),$$

$$n_1=c/b\,\{1+(c/bn_2-1)\,e^{c\tau}\},$$

and $$c/b=n_1+n_2.$$

Eliminating n_1 and n_2,

$$\tanh\frac{c\tau}{4}=\frac{\gamma}{c}\tan\frac{\gamma\tau}{4} \qquad \text{.....(12).}$$

Substituting $\gamma=\sqrt{(4ab-c^2)}$,

$$\tanh\frac{c\tau}{4}=\sqrt{\left(\frac{4ab}{c^2}-1\right)}\tan\left\{\frac{c\tau}{4}\sqrt{\left(\frac{4ab}{c^2}-1\right)}\right\}.$$

Approximating,

$$\tanh\frac{c\tau}{4}=\left(\frac{4ab}{c^2}-1\right)\frac{c\tau}{4} \qquad \text{.....(13).}$$

For values of $c\tau/4$ small compared with unity, equation (13) reduces to

$$a = c^2/2b.$$

When $c\tau/4$ is large compared with unity, equation (13) reduces to

$$a = c^2/4b.$$

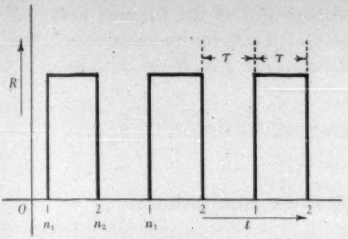

Figure 5.

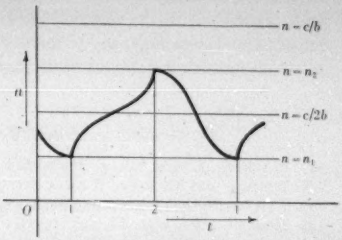

Figure 6.

It follows that the variation of a with frequency should be as shown in figure 7 and that the igniting power of a high-frequency discharge should be approximately half that of a low-frequency discharge of similar energy. This is found to be true in practice. Finch and Thompson's[13] results for mixtures of carbon monoxide with air are shown graphically in figure 8.

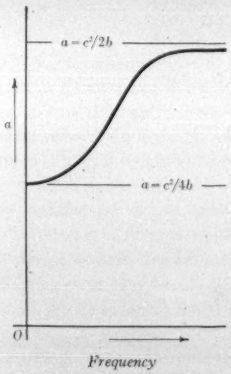

Figure 7.

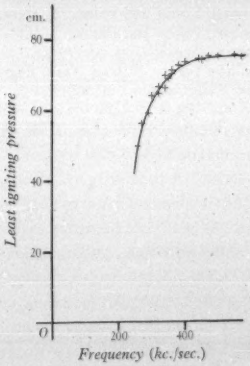

Figure 8.

Equation (13) can be used in conjunction with the experimental results of figure 8 to calculate an approximate value for ω, the average life of an activated molecule. At the point where $a \doteqdot 1{\cdot}7c^2/4b$, equation (13) gives $c\tau/4 = 1$ or $\omega = 1/8f$, where f is the frequency of the discharge. For carbon monoxide at atmospheric pressure the life of an activated molecule suitably excited for ignition should there-

fore be of the order of 0·4 microsecond. The lives of activated molecules in metastable states of excitation are well known to be of this order[18, 19].

§ 5. ACKNOWLEDGEMENT

The author wishes to record his high appreciation of the experience gained from work carried out in the electrochemistry laboratories of the Imperial College of Science and Technology, and to thank Prof. G. I. Finch for his valuable assistance in connexion with the subject of the paper.

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A SELF-SYNCHRONIZING TIME BASE FOR THE DISTANT OBSERVATION OF WIRELESS PULSE TRANSMISSIONS

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ABSTRACT. A circuit is described for producing in a cathode-ray oscillograph a time base suitable for the investigation of wireless pulses reflected from the ionosphere when no ground wave is present. The time base is locked to the received groups of echoes and gives a stationary pattern on the oscillograph even when all the echoes are fading considerably. The whole group of echoes, including the first, is delineated on a portion of the time base which is not obscured by end effects in the trace, so that accurate measurements of time intervals can be made.

§ 1. INTRODUCTION

In using pulse-transmissions of the Breit and Tuve type for the study of the ionosphere it has been usual to place the receiving station close to the transmitter, so that the received wave consisted of a strong ground wave followed by one or more echoes from the reflecting regions. Under these conditions the time base of the oscillograph can be readily synchronized with the recurrence frequency of the transmitted pulses either by operating both from the same a.c. supply mains[1], or else by making use of the constant-amplitude ground wave as a synchronizing impulse[2]. When it is desired to observe pulses returned from the ionosphere to a distant receiving station these methods of synchronizing cannot be employed, since the supply mains at two widely separated places always exhibit some slight drift of phase and, further, for all but the smallest distances the ground wave is too weak to be received. A modified form of time base has therefore been developed for distant working, the requirements for which may be summarized as follows. (1) The time-base traverse should be locked to the received groups of echoes (there being more than one echo in general for each transmitted pulse) so as to give a stationary pattern on the oscillograph, even when all the echoes are fading considerably. (2) In order that relative times of arrival may be measured accurately for the several echoes, the whole group including the first, perhaps weak, echo should be delineated on a portion of the time base which is not obscured by end effects in the trace.

The apparatus described below, which is based on a design due to Scholz[3], has been found to fulfil these two conditions well, and with it measurements of the time spacing between the arrival of echoes at a distant station have been made with considerable accuracy.

§ 2. THE CIRCUIT ARRANGEMENT

The transmitted pulses were sent at a recurrence frequency of 50 c./sec. and the method employed to ensure that the first echo should not be obscured at the end of the oscillograph trace was to operate the receiver time base at a repetition frequency of 25 c./sec., thus allowing one group of echoes to be used for starting the time base while the next appeared, in a convenient form for measurement, on an undistorted part of the trace.

A thyratron was employed for controlling the time base, the circuit details of which are shown in figure 1. The diode detector of the receiving amplifier is wired to give a positive voltage output relative to earth and this is fed to the grid of valve V_1, the anode of which provides the echo voltage for the vertical deflecting plates of the oscillograph. Part of this same potential is passed to the grid of V_2 in

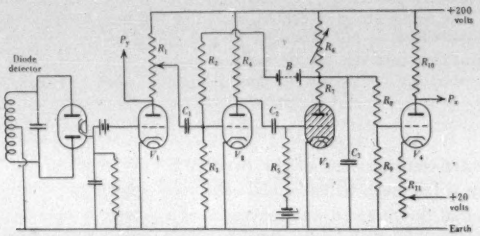

Figure 1.

the form of negative impulses, and from there to the grid of the thyratron V_3, where it appears as positive impulses. The thyratron is arranged as a relaxation oscillator by virtue of the condenser and resistance C_3 and R_8, and its frequency is adjusted to be close to 25 c./sec. Its anode-potential therefore rises gradually from the extinguishing potential of about 15 V. to the striking potential (which is determined by its grid bias) of about 100 V. Half of this potential-variation is applied through the biasing battery B to the grid of the previous valve V_2, where it has the effect of desensitizing this valve for all but the last part of the potential-rise. Since the signal voltage impulses on the grid of V_2 are negative in relation to earth, it is clear that during the desensitized period they can have no effect at its anode, however strong the echoes may be. The battery voltage B is made equal to about 90 V., so that only when the condenser C_3 has charged up to close on this value will the valve V_2 begin passing current. Immediately it becomes conducting, the impulses on its grid appear as positive pulses at its anode, and the first of these, unless extremely weak, will cause the thyratron to strike. In this way the thyratron

oscillation is made to lock stably to alternate groups of echoes even when the relative amplitudes of the different echoes are varying considerably with time.

The anode-potential of the thyratron does not provide a suitable time base for observing the alternate groups of echoes since the whole of each group arrives within a voltage-rise of only about 10 V., occurring when the potential difference across C_3 is at about half its final value. It is necessary therefore to amplify this portion alone of the time-base, so that the echo pattern can be made to cover a reasonably large portion of the oscillograph screen. This is done by means of the valve V_4, which has a variable positive voltage of about 20 V. on its cathode. It therefore begins to conduct only when the voltage on its grid approaches this value, i.e. when the condenser-voltage approaches twice this value, since the resistances R_8 and R_9 are equal in magnitude. After this the current in the valve rises rapidly to saturation, and then remains constant for the rest of the voltage-rise. The anode-potential of this valve provides the horizontal deflection on the oscillograph, and the magnitude of the voltage-rise on C_3 which is embraced by its active period is controlled by a cathode resistance R_{11}.

Although the rise of voltage across C_3 occurs exponentially with time, the portion, extending over about 10 V., which is amplified by V_4 is almost linear, so that by choosing a good triode for this amplifier the resulting time base can be made very nearly linear. It will be seen that the curvatures introduced by the exponential rise and by non-linearity in the valve characteristic are opposing, and it was found in practice that the second was the more important. It was found, however, that by connecting a shunt resistance across the condenser, and so exaggerating slightly the exponential effect, the two curvatures could be made to cancel with considerable precision, and thus a time base which was linear over its whole range within the accuracy of measurement was obtained. The resistance used for this, not shown in the figure, was 50,000 Ω.

Care was necessary in choosing values for the condenser and resistance coupling between V_1 and V_2 in order that the desensitizing bias should be applied effectively to V_2 through the grid resistance R_2, while the pulses were passed on from the anode of V_1 without serious loss of amplitude. A suitable time constant for the grid leak and condenser was found to be 0·0025 sec.

The values used for the important components in the apparatus were as follows:

R_1, 50,000 Ω.; R_2, 1 MΩ.; R_3, 1 MΩ.; R_4, 50,000 Ω.; R_5, 100,000 Ω.; R_6, 100,000 Ω.; R_7, 300 Ω.; R_8, 100,000 Ω.; R_9, 100,000 Ω.; R_{10}, 30,000 Ω.; R_{11}, 10,000 Ω.; C_1, 0·005 μF.; C_2, 0·001 μF.; C_3, 0·6 μF.

Both the receiving amplifier and the time-base apparatus incorporated a.c. mains-operated valves, and the high-tension supply was obtained from a rectifier. It is of interest, therefore, to note that the circuit showed no tendency to lock to the local frequency instead of to the received pulses.

A 750-c./sec. oscillator was used for calibration of the time-base speed, the oscillation being applied in place of the signal voltages to the oscillograph when required. In order that a stationary curve should be formed on the screen the

oscillator had to be locked to the signal-recurrence frequency, and this was accomplished by using, as a dynatron oscillator, a screen-grid valve the control grid of which was loosely coupled to the thyratron anode. The sudden discharges of the latter provided a sufficiently strong 30th harmonic to ensure stable locking, and the method of electron coupling avoided any reaction back from the oscillator to the time-base circuits.

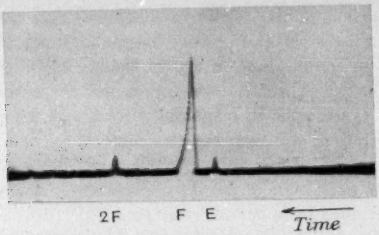

Figure 2.

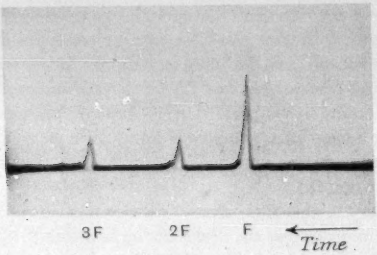

Figure 3.

The apparatus has been used in a number of experiments on the oblique reflection of waves from the ionosphere, an account of which is being published elsewhere. Figures 2 and 3 show two typical echo patterns obtained with the receiving apparatus at Cambridge, with in this case a distant (unknown) transmission on a wave-length of 80 m. There is no ground wave, and it is seen that in the first picture a weak *E* echo is present together with the first- and second-order *F* reflections, while in the second only *F* echoes are received.

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A PHOTOELECTRIC SPECTROPHOTOMETER OF HIGH ACCURACY

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ABSTRACT. Details are given concerning the components used in constructing a photoelectric spectrophotometer employing as light-sensitive element a vacuum emission photocell of a modern type with central plate cathode. It is claimed that the instrument as a whole has a linear response over the necessary range of photocurrents and the method by which this property was tested is described. The instrument has been applied to the measurement of spectral transmissions of the International Standard Blue Filter R 3.28 and the results, which are in good agreement with the internationally adopted figures, are given in full. The effect of temperature on this filter is shown also.

§ 1. INTRODUCTION

Until recently attempts to use the emission photocell as a direct measuring instrument have not met with entire sucess owing to the fact that even if stability was ensured by the use of vacuum cells, these cells frequently did not give a linear response to variable illumination. Various methods of avoiding this and other possible defects in the photocell have been tried, depending generally on the use of the photocell merely to obtain a balance between two illuminations (usually of identical spectral composition), instead of to measure one of them directly in terms of photocurrent. These methods, while having very definite advantages in eliminating the effects of undesirable features in the photocell, have other practical disadvantages, optical and electrical.

However, it has now become possible to obtain emission photocells of the vacuum type which have a sensibly linear {illumination, current} characteristic, at least in the region of photocurrents likely to be concerned in the case of spectrophotometry, say from 5.10^{-10} A. downward. Thus, while from the purely philosophical point of view methods of spectrophotometry such as those already mentioned may be the more fundamental, the direct use of the photocell as the measuring instrument nevertheless becomes possible. Even if a complicated electrical circuit still remains necessary, reliability and simplicity of operation then show a marked gain, as compared with the indirect methods.

The features chiefly desired in a direct-reading photoelectric spectrophotometer are (1) linear performance of the instrument as a whole, (2) obedience to Talbot's

law if possible, (3) good sensitivity, (4) electrical and mechanical stability, and (5) avoidance of stray light in the beam incident on the test filter. The second feature may be dispensed with provided a rigorous demonstration of the first is possible.

The object of the present paper is to describe a spectrophotometer which satisfies at least the requirements (1), (3), (4) and (5), and the method by which its linearity was tested at any desired wave-length. Results obtained with it are quoted and compared with those obtained by other methods. No novelty is claimed in respect of either the optical or the electrical principles embodied in the instrument, but since its satisfactory assembly and operation depend almost entirely on strict attention to technical details, these are fully set out.

§ 2. THE OPTICAL SYSTEM

The monochromator. The optical system is shown in figure 1. The nucleus of the system is an Adam Hilger constant-deviation spectrometer of aperture about F/11. In the instrument used by the authors the telescope slit is symmetrical, while the collimator slit is not. For convenience, both slits should be symmetrical.

The source of light. The source of light S is a Siemens 12-volt 48-watt gas-filled lamp of commercial type, with a single-pillar coiled filament having no supports other than the leading-in wires. The lamp is burned cap down. This lamp may be run for long periods at 13·5 V. It was found more satisfactory as regards available light and steadiness than either a gas-filled strip-filament lamp, or other lamps of the projection type. Moreover, the filament is stout enough not to become distorted appreciably over moderate periods of time, even if run at 13·5 V.

The condensing lens. The system used to focus an image of the light-source on the collimator slit need not have an aperture greater than that of the spectrometer. To avoid loss of light by reflection the number of glass surfaces should be a minimum. In practice an achromatic doublet L_1 of focal length about 10 cm. and diameter 3·5 cm. is used, the distance from lens to lamp filament being 17 cm. and that from lens to slit 25 cm. Appropriate light screens are used and are shown in figure 1. The image of the lamp filament should, of course, be larger than the collimator slit to obtain the maximum available light.

The mechanical supports. Since absolute rigidity of the optical system is essential to maintain constant the light entering the system, the lens and light source are mounted on a piece of stout aluminium of L-section attached to the spectrometer bedplate. The spectrometer and also the remainder of the optical and electrical systems mentioned below, except batteries, galvanometer, and potentiometer, are clamped down to a slate slab.

The exit lens. The lens L_2 is used to receive the light emerging from the telescope slit and to render it parallel for transmission through the test filter. Its focal length may suitably be 15 cm. and its aperture at least that of the spectrometer system. It is placed at its focal length from the telescope slit and thus throws light on an area of the photocell cathode of shape similar to the section of the light beam

entering the telescope lens. By suitable choice of the focal length of this lens this illuminated area is made nearly large enough to extend to the edges of the cathode.

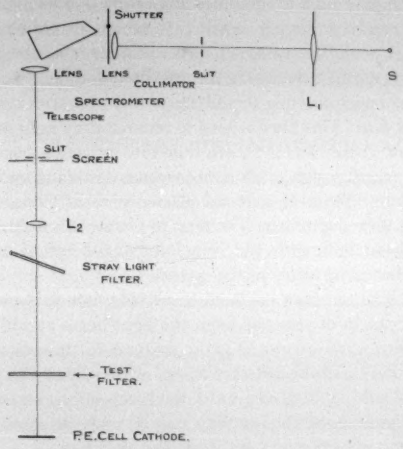

Figure 1. Diagrammatic plan of optical system.

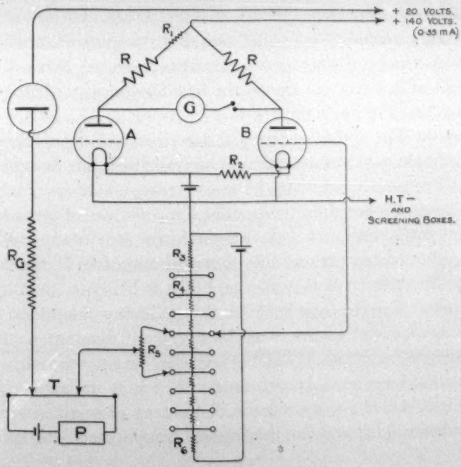

Figure 2. Electrical circuit.

The exit lens is tilted very slightly from the normal position so as to avoid inter-reflections between the components of the system.

The reasons for adopting this exit system are that it is simple, as regards number of lenses required, and absorption is consequently low; it gives a patch of light on the cell cathode large enough to minimize any errors due to slight displacement of the patch over areas of varying sensitivity, which displacement may possibly occur when a thick or slightly wedge-shaped test filter is in use; and it gives minimum divergence of the light traversing the test filter, and hence minimum error due to obliquity of the rays traversing this filter.

The stray-light filter. This filter is used to remove stray light of unwanted wavelengths from the exit beam, and is chosen therefore to have a principal transmission band in the wave-length region where a measurement is being undertaken, and high absorption elsewhere. A set of coloured glasses such as Chance's is useful from which to choose a stray-light filter. The filter is placed in a holder 3 or 4 cm. from the exit lens as shown in figure 1 and is inclined to the optical axis to avoid interreflection with other components of the system.

The test filter. The test filter is placed in a holder which is movable so that the filter may be inserted in or removed from the light beam at will. Care should be taken that this filter shall be also slightly inclined to the axis of the system, to avoid the formation of a strong reflected image of the slit on the metal work of the slit. This image should be displaced on to the black screen shown in figure 1 and so absorbed. The position for the test filter may suitably be about 8–10 cm. behind the stray-light filter and say 12–15 cm. from the photocell.

The photocell. The final component of the optical system is the photocell. The type of cell chosen was an Osram KMV 6. This cell has the advantages that the cathode is an easily visible metal plate, and that its spectral sensitivity makes it suitable for measurements throughout the visible spectrum. It has also been found that selected cells of this type are among the best for linearity of characteristic, and that they have good electrical stability.

General remarks. The optical system just described and shown diagrammatically in figure 1 was chosen to secure a maximum of available light. It is believed that all the precautions necessary to exclude the most common sources of error have been taken. It is to be remembered, however, that some sources of error may still arise. For instance the interposition of a thick filter in the exit beam may alter slightly the size of the illuminated area of the photocell cathode. If the cathode is not uniformly sensitive some error may accrue, but it is likely to be much less than if the filter were inserted in the light beam on the collimator side of the spectrometer, with possible displacement of the image of the lamp filament on the collimator slit.

The condensing lens must be achromatic and it is an advantage as regards focusing if the exit lens also is achromatic. Too many glass-air interfaces seriously reduce the available light, and for this reason complicated lens systems are undesirable.

Temperature-control may be necessary for the measurement of filters of certain classes, but is not dealt with here. Change in temperature of the test filter due to absorbed radiation will not, however, be so serious in the present instrument as in

cases where the test filter is interposed in the more intense beam of light between the source and the collimator.

Finally, it is advisable so to design the system that no outside illumination falls on the photocell during the shifting of filters. Insertion of the test filter and the opening and closing of the shutter on the spectrometer is conveniently done with Bowden wire controls. Familiarity with the necessary precautions in the calibration and use of the spectrometer is assumed throughout this paper.

§ 3. THE ELECTRICAL SYSTEM

The circuit. This is shown diagrammatically in figure 2. It is the well-known valve-bridge circuit and differs in no essentials from that used by previous workers[1, 2]. Compensation of both filament and anode circuits is provided for, to render the balance of the bridge independent of variations of battery voltage. Control of the voltage on both grids over a small range is also possible, apart from the separate voltage-control used on the grid connected with the photocell for purposes of measurement.

Thermionic valve unit. The valves, of Mullard type PM1A, were supplied as a matched pair by the makers. The wisdom of using dull-emitter valves of general-service type in a set-up of high sensitivity may be doubted, but the authors believe that the circuit described here is as stable as a circuit of comparable sensitivity using pliotrons or electrometer valves. Good amplification is obtained with a comparatively low grid resistance, while the total anode current is less than 0·4 mA. The main difference is that the poorer grid insulation in the case of the PM1A valve makes it unsuitable for a rate-of-charge method. The deflection sensitivity is however at least as great as that of the circuit described by Dubridge[3], in which pliotrons were used (see Appendix).

The two PM1A valves are uncapped and fixed in holes in a wax block, the cap end projecting uppermost, by melting wax round the tops of the bulbs. By the use of stiff wire and terminals melted into the sides of the wax block, the resistors R, R, R_1 and R_2 are made independent of any other support. Six terminals are used and serve respectively for the filament supply (two), the galvanometer leads (two), the h.-t. supply (one), and the grid control on valve B (one).

Anode resistors. The anode resistors R, each of 700,000 ohms, are Karbowid resistors, type 2*b*, supplied by Messrs Siemens-Schuckert. Though not wire-wound these resistors are stable and have a low temperature coefficient.

Compensating resistors. The resistor R_1 may well be a Karbowid resistor of suitable value, determined as described below. It may have to be inserted in either anode circuit according to the direction in which compensation is found to be required. R_2 is a wire resistor with soldered tappings, and is conveniently wound on a short length of ebonite rod. Its actual value—probably a few ohms—is determined as described below.

Grid resistor. This resistor R_G is of special design, and consists of ninety 5-megohm resistors of Karbowid type 2*b* connected in series and embedded entirely in a single block of paraffin wax. For reasons of brevity the method of achieving

this form of assembly cannot be given here, but it should be noted that heating of the wax to a temperature above that of boiling water is to be avoided. This grid resistor unit is mechanically rigid, and is free from rapid temperature-changes and changes in insulation resistance. These three are all essential requirements. The unit is undoubtedly more stable than a liquid resistance of the same order. The number of resistors available when the unit was made up led to the value of 450 megohms rather than the round value 500 megohms.*

The grid-control unit. The unit comprising the resistances R_3, R_4, R_5 and R_6 serves to control the grid potentials of the two valves in order to set these at a pre-selected value, and to bring the bridge into balance with the photocell obscured. The resistances R_3, R_4 and R_6 are constantan coils of 26 s.w.g. Their values are R_3 25 ohms, R_6 160 ohms, and each of the eight coils R_4 2 ohms. The end points of the 2-ohm coils are brought out each to a pair of sockets. A single wander plug selects the grid potential for valve B, no fine adjustment being provided. Vernier adjustment for valve A is obtainable by means of R_5. This is a drum type continuously variable potential divider of resistance 4·5 ohms, which may be plugged across any consecutive pair of 2-ohm coils. It will be seen quite simply that if the whole unit is connected to a 2-V. cell as shown, the grid potentials are adjustable between about $-0{\cdot}25$ and $-0{\cdot}4$ V. relative to the negative filament lead, a range sufficient to ensure that the bridge shall be capable of being balanced provided the valves are matched. The reason for the choice of this range is given in § 4.

The measuring-instrument. The actual measuring-instrument of the system is a Tinsley general utility potentiometer T of resistance 40 ohms used as a potential divider and fed from a 2-V. cell in series with a plug box P. The latter serves to adjust the current in the potentiometer to any desired value, so that the scaling of the instrument can be adjusted to suit the order of photocurrent obtaining in any given measurement. The potentiometer T is of course so connected that the potential applied by its means in the grid circuit of valve A opposes that due to the flow of photocurrent through R_G.

The bridge galvanometer. The galvanometer G is a Tinsley high-sensitivity reflecting galvanometer of resistance 4620 ohms used with the aperiodic connexion. A scale divided in millimetres is used at a distance of about 1 m. The sensitivity of this galvanometer is approximately 3000 mm. per μA. at 1 m.

Batteries. The batteries employed for the high-tension and photocell supplies are a 140-V. bank of Oldham accumulators of type LHTL of 5·5 ampere-hour capacity. The voltage on the photocell was 20. Two-volt cells of 24 ampere-hour capacity are used for the other supplies.

Assembly. On account of the high sensitivity it was thought desirable to adopt a screening system to minimize the effect of stray fields from other sources. The screening system is not, however, complete, the bridge galvanometer and key and the Tinsley potentiometer being unscreened, as a matter of convenience. The valve unit and grid resistor are housed in a metal box, while the photocell is behind these,

* 100 megohm resistors of type 2*b* can now be obtained but their suitability for this circuit has not been tested by the authors.

in a separate compartment, but connected to the valve grid by a wire passing through a small hole in the wall of the compartment. There is also an aperture in the front of this compartment just large enough to admit the light-beam to the photocell. A second separate screening-box holds the three 2-V. accumulators and grid-control unit, the latter being adjusted when necessary through a movable lid. A third metal box contains the high-tension accumulators. Connexions between the systems in the three screening boxes, and those leading to the Tinsley potentiometer are all made with lead-shielded cable, the lead covering being connected, with the boxes themselves, to the negative filament lead. There is no actual earth on the system. The leads to the galvanometer and key, and the key itself, must be well insulated. For this reason unscreened rubber-covered cable suspended in mid-air is used for this short section of wiring, and the key is fixed to a wax slab.

Determination of the values of R_1 and R_2 is carried out by trial[1,2]. Adjustments are made until the balance of the bridge is not appreciably upset by a small change in voltage of either high-tension or filament battery. An artificial change is suitably obtained by short-circuiting a resistor in the supply lead. After each adjustment of R_1 or R_2 it is, of course, necessary to re-balance the bridge by means of the grid-control unit, and it is preferable to adjust R_1 and R_2 alternately, starting with R_2, R_1 being zero at first.

§ 4. OPERATION

Operation of the valve A under conditions of zero grid current is found to eliminate unsteadiness which is observable when a finite grid current is flowing through the resistor R_G, and which is presumably due to fluctuations in this current. The appropriate setting of grid voltage to secure this condition is of course that for which the short-circuiting of R_G (with the photocell disconnected from the valve-grid) produces no effect on the balance of the circuit. It is determined simply by trial, and in the set-up described was found to lie in the neighbourhood of $-0{\cdot}3$ V. relative to the negative filament lead.

The whole electrical system should be switched on and roughly set to balance with the photocell obscured a couple of hours before measurements are to be made. The light source should be fed from batteries and should also be switched on some time previous to measurements. A means of observing the constancy of the operating voltage over the short period taken by one measurement is desirable. Meanwhile the slits of the spectrometer may be set to include the desired wave-length band.* An impurity of about 50 angstroms need not be exceeded with the set-up herein described. For maximum available light at a given spectral purity, the two slits are set at equal widths. To facilitate setting the slits without disturbing other apparatus it is useful to have a mirror or reflecting prism combined with the spectrometer eyepiece, which is inserted between the telescope slit and the lens L_2. The eye may then be placed to one side of the optical axis and observations of the slit made at right angles to the latter. The appropriate stray-light filter and the test filter are then placed in their respective holders, and the whole of the exit system

* If measurements are made over a range of wave-lengths, further slit-adjustments may be necessary to maintain the desired spectral purity and at the same time obtain the maximum available light.

is thoroughly screened with black velvet or a black box. The shutter of the spectrometer is then opened and the cell exposed for say 10 min. to the maximum illumination subsequently to be dealt with, the bridge being balanced by means of T. This tends to stabilize the effect of any drift in the photocell. Measurements should follow immediately.

The sequence of operations in the measurement of filter transmission is as follows. The desired wave-length is set on the spectrometer and the lamp voltage is maintained steady. With the shutter of the spectrometer closed and the potentiometer T set at zero the valve bridge is balanced to within a few millimetres on the galvanometer scale, by means of the control on the grid of valve A. The position of rest of the galvanometer spot with the key depressed is then taken as the null position for the following operations. With the test filter out of the beam; the spectrometer shutter is opened and the bridge rebalanced as rapidly as possible by means of potentiometer T only. The same operations are repeated with the test filter in the beam, and the ratio of the readings of T gives the filter transmission.

The current in T is, of course, set by trial to give a suitable scale reading by inserting resistance in the box P. Currents from 0·5 to 8 mA. were found suitable by the authors. It is advisable not to make a change in this current, however, during operation, unless its value has been set to the maximum during the steadying period of 2 hours preliminary to measurements. Further, it is inadvisable to leave the bridge out of balance for longer than necessary, as drift of the bridge is in that case experienced on resetting to balance.

§ 5. TEST FOR LINEARITY

The principle invoked in this test is that of the summation of a number of equal monochromatic light beams. If, say, five beams be projected separately or in combination on to the photocell, the measured effect of the five together should be equal to the sum of the measured effects of the five separate beams, provided that the cell has a linear characteristic. The application of the principle is not easy, however, because it is necessary for each beam to fall on the same area of the cathode and be distributed over that area in the same way. For instance, if a diaphragm with five holes be placed at the lens L_1 of figure 1 or between the collimator and telescope lenses, an image of the holes will be produced on the cathode of the cell, and the necessary requirements are not fulfilled. Close conformity to the necessary conditions is secured if the means used to subdivide the light into a number of separately controllable beams is situated in a focal plane of the system, and the photocell cathode and the telescope lens are arranged to be in conjugate planes with respect to the exit lens. Figure 3 shows how this is achieved. The same source S is used and a large condenser C forms an image of the filament about 4 cm. long at F. At F is situated a grid of six horizontal blackened narrow steel bars (double knife-edges) which can be clamped in any positions relative to each other. This grid cuts the filament image at F into five parts, and the positions of F and L_1 are arranged so that all these five parts are focused by means of L_1 upon the collimator slit. Now the five beams of light transmitted by the grid F eventually

reach the photocell as monochromatic beams of almost identical distribution, but of slightly different incidence upon the cathode. They can be allowed so to reach it either individually or in groups by means of suitable shutters at *F*. To render the effects of the five beams equal, the positions of the bars of the grid are adjusted by trial and error. For this purpose it is convenient to bridge them across the poles of a flat U-shaped magnet to which they adhere. When the correct positions have been found, the bars are clamped in place. The shutters may then consist of two pieces of thin tin plate, blackened, which will also adhere in any desired position, and may be moved easily without disturbing the position of the grid. The whole optical system must be as rigid as possible.

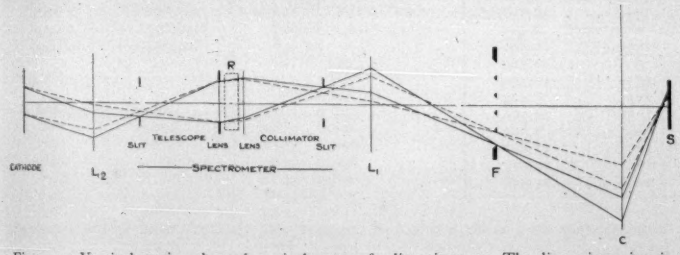

Figure 3. Vertical section through optical system for linearity tests. The dispersive prism is indicated by rectangle *R*. (This diagram is not drawn to scale.)

To test for linearity the spectrometer is set to the desired wave-length, the slits are opened to a suitable value, and the grid *F* adjusted as described above and then clamped. Measurements are made in the usual way on the five light-beams separately and then on groups up to the five together. It is perhaps useful to repeat measurements on the five beams together several times during the series as a check or to provide a sliding scale of corrections.

For this test the slits should of course be set wide enough to give readings covering the range normally employed in spectrophotometric measurements. There is no objection to this since spectral purity is not of first importance.

Table 1 gives a typical set of results.

The figures in the column headed "ratio" show that the whole set-up is linear at wave-length 4400 A. to a few parts in 10,000. The particular cell and set-up used by the authors gives similar results throughout the visible spectrum, and over the range of photocurrents employed by them.

§6. SPECTROPHOTOMETRIC RESULTS

Two separate tables of results, with comparative figures from other sources, are given below in illustration of the performance of the instrument. A signal-green glass affords a fairly stringent test of such an instrument, both as regards working at the blue end of the spectrum where there is not much available energy, and as regards the efficiency of the system of stray-light filters. Accordingly a glass

Table 1. λ, 4400 A. Spectral impurity, approximately 80 A. Lamp voltage, 13·5. Current in potentiometer *T*, 2 mA.

Beams	Reading	Summary (corrected)			
		Beams	Reading	Added value	Ratio
1–5	12,594	1	2,183	—	—
1	2,183	2	2,802	—	—
1–5	12,596	3	2,628	—	—
2	2,802	4	2,462	—	—
1–5	12,599	5	2,519	—	—
3	2,628	2–3	5,428	5,430	1·0003
1–5	12,597	2–4	7,891	7,892	1·0002
4	2,462	1–4	10,077	10,075	0·9998
1–5	12,598	1–5	12,596	12,594	0·9999
5	2,519				
1–5	12,599				
2–3	5,429				
1–5	12,598				
2–4	7,892				
1–5	12,597				
1–4	10,077				
1–5	12,596				

of this type was used as the subject of the first test, the results of which are shown in table 2.

Table 2. Test filter, B.T. light green 501 N.P.L. 1924. Wave-band, not greater than 50 A. Temperature, 20° C.

λ in μ	Transmission observed			
	Photoelectrically 1st set	2nd set	Visually (N.P.L. Optics Division)	Percentage difference
0·40	0·224	0·224	0·224	0
0·41	0·274	0·275	0·274	0
0·42	0·322	0·322	0·322	0
0·43	—	—	0·365	—
0·44	0·411	0·411	0·408	+0·7
0·46	0·480	0·479	0·476	+0·8
0·48	0·519	0·519	0·512	+1·3
0·50	0·515	0·515	0·509	+1·2
0·52	0·448	0·448	0·449	−0·2
0·54	0·328	0·329	0·328	0
0·56	0·1993	0·1998	0·199	+0·3
0·58	0·1000	0·1005	0·1011	−0·9
0·60	0·0444	0·0444	0·0445	−0·2
0·62	0·0180	0·0179	0·0182	−1·1
0·64	$0{\cdot}0068_2$	$0{\cdot}0068_0$	0·0070	−2·8

Calculated integral transmissions for colour temperature 2360° K. are 0·1649 based on photoelectric readings and 0·1649 based on visual readings.

The agreement between the two sets of results is satisfactory, but it was unfortunate that this particular glass, although carefully worked, was not strictly uniform in density over its area. Despite careful centring of the filter in each case, it is probable that the discrepancies shown in the last column of the table are due, at least in part, to this fact.

The second set of results refers to a pale blue glass of the cobalt type which forms one of a set of four photometric filters now distributed among the four national standardizing laboratories. The transmission values of these filters have been the subject of international comparison and agreement[4]. Table 3 gives the mean values obtained at the Bureau of Standards by K. S. Gibson for filter R 3.28, together with the present authors' results obtained more recently on the same filter with the instrument above described. The glasses used as stray-light filters in the latter measurements are indicated also.

Table 3. Spectral transmission of filter R 3.28.

λ in μ	*Gibson's mean values (1929 and 1932)	Preston and Cuckow's photoelectric determinations (1936)			Stray-light filter
		At 16° C.		At 26° C.	
		Two sets		One set	
0·40	0·902	0·903	0·902	0·902	Purple
0·41	0·896	0·897	0·896	0·894	,,
0·42	0·886	0·883	0·886	0·885	,,
0·43	0·876	0·874	0·876	0·874	Thin cobalt blue
0·44	0·866	0·867	0·866	0·865	,,
0·45	0·856	0·857	0·857	0·854	,,
0·46	0·842	0·842	0·843	0·841	,,
0·47	0·816	0·816	0·816	0·814	Blue-green
0·48	0·778	0·780	0·780	0·778	,,
0·49	0·732	0·735	0·735	0·734	,,
0·50	0·694	0·696	0·696	0·695	,,
0·51	0·643	0·644	0·644	0·644	,,
0·52	0·594	0·597	0·597	0·596	,,
0·53	0·556	0·556	0·556	0·557	Green
0·54	0·557	0·557	0·556	0·557	,,
0·55	0·596	0·596	0·596	0·596	,,
0·56	0·619	0·618	0·618	0·619	,,
0·57	0·579	0·578	0·578	0·579	Light orange
0·58	0·499	0·498	0·498	0·501	,,
0·59	0·437	0·435	0·435	0·437	,,
0·60	0·441	0·441	0·441	0·442	,,
0·61	0·457	0·458	0·458	0·458	,,
0·62	0·463	0·464	0·464	0·465	,,
0·63	0·459	0·458	0·458	0·459	,,
0·64	0·448	0·448	0·448	0·449	Selenium red
0·65	0·455	0·457	0·457	0·457	,,
0·66	0·490	0·496	0·495	0·494	,,
0·67	0·561	0·567	0·567	0·562	,,
0·68	0·657	0·665	0·666	0·657	,,
0·69	0·762	0·766	0·766	0·759	,,
0·70	0·835	0·840	0·839	0·835	,,
0·71	0·875	0·876	0·875	0·873	,,
0·72	0·893	0·893	0·892	0·890	,,
0·73	0·900	0·899	0·899	0·898	,,
0·74	0·902	0·903	0·900	0·900	,,

* *P.V. Com. int. Poids Mes.* **16**, 320 (1933).

In the case of the determinations made by the present authors the wave-band used was nowhere greater than 50 A., and in the main it was considerably less. Slit-width corrections are, therefore, in no case large enough to be taken into account. The calculated integral transmissions for colour temperature 2080° K.,

using the international relative-luminosity factors are 0·5239 based on Gibson's mean data, 0·5237 based on the present authors' photoelectric determination at 16° C., 0·5245 based on the present authors' photoelectric determination at 26° C., and 0·5235 for the internationally agreed value[4].*

The differences between the present authors' photoelectric values at 26° C. and Gibson's mean values (which also apply to a temperature of approximately 26° C.) are everywhere small, the greatest deviation being 0·8 per cent at $\lambda = 0{\cdot}66\,\mu$ and the average deviation 0·2 per cent. The present authors' determinations also confirm the temperature effect between $\lambda = 0{\cdot}66\,\mu$ and $\lambda = 0{\cdot}72\,\mu$, as noted by Gibson. Changes in this region do not, however, greatly influence the integral transmission.

§7. CONCLUSION

The results so far obtained with the instrument described suggest that it compares favourably with the best visual methods as regards both precision and absolute accuracy. The former is not difficult to attain, in general, with photoelectric instruments; the latter, on the other hand, is usually the main problem. The authors believe it has been solved by employing a type of photocell which possesses almost all of the features desirable from the photometric standpoint, coupled with a stringent method of testing for linearity of the illumination-current characteristic, and close attention to details of design in regard to the electrical circuits and optical train.

APPENDIX: SOME FIGURES RELATING TO PERFORMANCE

The whole instrument, used under the conditions described above, has been found to be stable as regards short-period fluctuations to within a 1-mm. deflection of the bridge galvanometer. It is also almost free from drift if the compensation of the bridge is carefully carried out. This stability is combined with an effective deflection sensitivity of 500,000 mm. per volt on the grid of valve *A*, a performance which compares favourably with that of a circuit described by Dubridge[3] in which pliotron or electrometer type valves are used. The present authors consider that little advantage is gained by the use of electrometer valves except when a rate-of-charge method is employed, or the very highest sensitivity is aimed at by the use of grid resistors of very high values. The present set-up is not primarily suitable for the rate-of-charge method since the insulation of the valve electrodes is inadequate. The sensitivity mentioned above is equivalent to a galvanometer deflection of 10 mm. for a photocurrent of $5 \cdot 10^{-14}$ A.

* The internationally agreed value of integral transmission is based on the mean spectrophotometric results obtained by the National Laboratories on the group of four filters, together with comparative measurements of integral transmission. The Bureau of Standards spectrophotometric values are quoted in the present paper as representative of these spectrophotometric results.

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MY RECENT PROGRESS IN GAS CALORIMETRY

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The Nineteenth Guthrie Lecture, delivered May 4, 1934

I desire in the first place to express to the Physical Society my appreciation of the honour they have done me in inviting me to deliver the Guthrie Lecture. This is an honour which anyone would value, but in my case there is the very special reason for my gratification that I knew Guthrie so well. I owe much to Guthrie. After I had been for a short time at a colliery he brought me back to South Kensington and made me at first his private assistant, and he gave me a life membership of this Society. For the last eight or nine years of his life I was in effect his right hand, and I know more of his ideas and ideals than anyone now living, unless it be his widow whom we welcome here this afternoon. I feel it a duty I owe to this Society to express these ideas, but more especially to the youngest members present. Let me tell you as best I can what Guthrie's feelings were, but in my own words if you will allow a long alliteration. The making of specious scientific surmises unsupported by experiment, however amusing it may be as a pastime or however loudly it may be advertised, does nothing to advance the certain knowledge of the world. The acid test of experiment is essential. So will you who in years to come will have the management of this Society in your hands accept this as a solemn message from the dead. If you would be true to the ideals of Guthrie you will seek for a Guthrie lecturer from among those who have done things rather than from those who have merely talked. *Nullius in verba* is the motto of the Royal Society.

Coming now to the subject of this lecture, the class of calorimeter which alone has been found suitable for examining the calorific value of gas as supplied for public consumption is that known as the water-flow calorimeter, that is, a stream of water is heated by the combustion of a stream of gas. If then the strengths of the two streams are known, and the rise of temperature, the calorific value can be deduced. The water-flow calorimeter was invented by Mr F. W. Hartley of the firm of Messrs Alexander Wright and Co. in the year 1882. When in the year 1905 tests for information on the calorific value of gas had to be instituted I examined three makes of instrument which were developments of Hartley's original calorimeter, but found that in each of them the mercury column in the hot thermometer was jumping about through two or three divisions—tenths of a degree—incessantly, and in consequence these instruments were quite unsuited for tests even for information. I accordingly invented and made the calorimeter known in every gas works in the country affectionately or otherwise as the "Boys", and in this for the first time there was an almost perfectly steady hot-thermometer reading[1]. When in

the year 1920 calorimeter tests superseded illuminating-power tests of gas, the Boys instrument was the best available, and it has carried a heavier burden since then than that for which it was originally designed. I have never considered it all that a calorimeter should be. There are two faults: (1) the acid gases and products of combustion dissolve away the base metal of which the parts are made, and repairs are needed every few years; (2) the instrument is sensitive to unsuitable conditions of use, and special precautions have to be taken to maintain suitable temperatures of the circulating water and surrounding air. Ever since 1920 I have desired to design a calorimeter free from these disadvantages and in other respects as perfect as possible. That used in my recording calorimeter goes only a small way in this direction, and though more particularly in the last ten years I have devoted myself to the design and construction of such an instrument, it was only about a year and a half ago that the unit which I am going to describe later to-day finally emerged, and with this I am satisfied.

Calorimeters are generally used for spot tests, that is, the thermometers are read, gas and water-flows determined, and calorific value deduced, but the greater problem is that of the recording calorimeter in which these operations are performed continuously and automatically and the result through all the hours of the day and night is expressed as a curve. It was this wider problem which mainly occupied me for a few years from the year 1920 and the result, when made without leaking joints and to my design, is quite satisfactory. I am not here, however, to go into any ancient history, but to tell you only about my recent progress in this engaging subject. If you wish to know anything about existing calorimeters you will find a complete and authoritative account in the standard book on the subject, a copy of which should be available in every physical laboratory[2].

You will appreciate that in the spring of last year I must have become fairly saturated with ideas on the subject. I had just completed the construction of the calorimeter unit which I have here this afternoon, and I then intended to graft on to it my water-weighing balance which automatically weighs out the required amount of water every half-minute, and an automatic meter governed by the thinking machine for providing always the same amount of gas corrected for temperature and pressure and water vapour. These elements worked perfectly and I did not seek to improve them or even to simplify them, as that did not seem likely to be possible, and in that frame of mind, without seeking for it, I had a dream on the 4th of May 1933, or saw a vision, call it what you will, but from nowhere there came in the night the unlooked for idea of a tube bent to a right angle rotating about one limb as an axis and carrying a bulb at the end of the other. This as it revolved dipped into water and as it turned the water ran out at the hollow axle. Well, that does not seem much of an invention, for I expect it is as old as the hills, but the interest as I see it now is the impression it made as being of real value. It was evident that it possessed the merit of having no internal working parts. It would go round and round for ever. I was sufficiently impressed by it to get up at six and go to Victoria Street where I blew in glass the bulb and tube you now see. Later, on considering it, the question arose—could the primitive idea be so developed

as to produce something of real value? I do not think I should have developed the theory of what I have running here now if it had not been for the stimulus afforded by that dream, and having developed it and being invited to deliver this lecture I looked anxiously at the calendar to see if the 4th of May should happen to be on a Friday. That settled the date of this lecture.

In any recording calorimeter, provision must be made for dealing with two kinds of variation. The first is that gas in different places is intended to have different values. If the temperature-rise is, as is most convenient, always to be the same if the gas is right, more water should be used with a richer gas. This is a mere matter of gearing, and to the Physical Society I need say no more about this. The real difficulty has always been the varying volume occupied by a gas saturated with water vapour at different temperatures and pressures, for equal volumes as indicated by a meter are not equal quantities. There are two ways of overcoming this difficulty. The first is the one which I adopted of causing the meter-speed to vary in proportion to the volume, which result I effected by means of the thinking machine; the other plan, used by the late Mr J. H. Fairweather, Chief Chemist to the Brentford Gas Company, was to alter the water-flow in the inverse ratio of the volume occupied by gas at any moment. Even though the thinking machine is one of the few elements in the different recording calorimeters at present in use which has never failed or given trouble, and I am by no means prepared to discard its use altogether, the development of the dream invention along these lines affords so elegant an example of applied geometry that it will I trust prove of interest to this Society.

What is required is that the quantity of water used should vary inversely as the gas-volume at the moment. Fortunately the range of variation is not great. In practice a range of 7 per cent above normal volume to 5 per cent below practically meets all requirements, but I have considered the larger range of 10 per cent either way.

In figure 1 I have drawn a hyperbola with a series of equally spaced ordinates, representing volumes from 0·5 to 2·0 by tenths and the corresponding abscissae. The lengths of the ordinates or the levels of the abscissae represent the depths of water in a uniform straight tube which would correspond to the reciprocals of the volumes. I have shaded the regions between $\pm$ 10 per cent, and between -5 per cent and $+7$ per cent, and have left the intervening portion of the diagram unshaded, for this is the really important part. I have drawn radial lines from the centre of curvature P of the hyperbola at its vertex to the intersections on the curve, and I have also drawn an arc of the circle of curvature at the vertex. You will notice that these radial lines corresponding to equal changes of volume are not equally spaced. They become progressively more close together as the volumes increase. This is not encouraging from the point of view of instrument-design. As you will see later, however, this progressive change is utilized. It occurred to me that if I used the reciprocal spacing for both sets of co-ordinates and cross-connected them in reversed order as you see in figure 2, I should get a curve which of necessity would be symmetrical about its axis OP, as it clearly is. In this the spacing of the radial lines

from P is widest at the sides and is a minimum in the middle, and being a minimum must in that region be very evenly spaced. I did not know what actual curve I should get and I have not found a curve generated in this way described anywhere. Mathematicians have related nearly everything with everything in nearly every kind of way, so that it might be expected that they had done this, as perhaps they have, yet it seems possible that no proper mathematician would deliberately do anything so illogical. Well, I wanted symmetry and I obtained it in this way, and the simple equation above the curve shows that it is a true hyperbola of half the

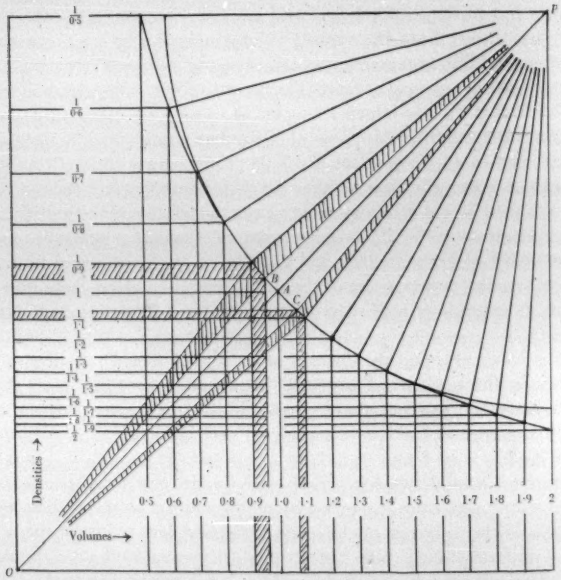

Figure 1.

size with its centre of curvature at P. There is an indication of its asymptotes at Q and of the negative branch at O. I have drawn also part of its circle of curvature at its vertex.

Now from the point of view of the instrument designer there is here something of real value. Suppose that a pointer centred at P, of length PA, is made to move through equal angles of the right magnitude by equal changes of gas volume, which is easy; then it will over the required range indicate a series of reciprocal levels with almost incredible accuracy.

The next step from indicating levels to making the water in a trough assume those levels is almost equally easy. A diagram of the mechanism to effect this is

given in figure 3. There is a balance arm *A* resting on a ball-bearing reel *B* carrying at one end a long air bell *C* in mercury and a pointer moving over a scale of gas volumes *D*. The immersion of the tube in the mercury is equivalent to a great stability such as would be produced by a heavy pendulum. This is balanced by the anti-gravity bob or negative pendulum *E* which can be adjusted exactly; a counter-weight *F* at the opposite end balances the air tube. When these two balance weights are correctly adjusted the balance arm will remain in neutral equilibrium in any position, even if the stop cock at the top of the air tube *C* is open. If however it

$$\left(\frac{1}{1+x}-\frac{1}{2}\right)\left(\frac{1}{1-x}-\frac{1}{2}\right)=\frac{2-(1+x)}{2(1+x)}\,\frac{2-(1-x)}{2(1-x)}=\frac{1}{4}\,\frac{(1-x)(1+x)}{(1+x)(1-x)}=\frac{1}{4}$$

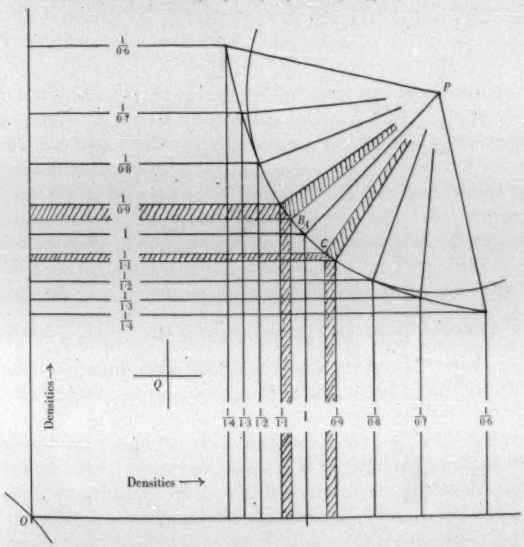

Figure 2.

is closed the bell will change its place as the air within expands or contracts and the actual volume if correctly set will remain so, and it may be read to about 1 part in 1000 on the scale. An identical scale on the air tube indicates the same volumes at the mercury-level, since the ratio

$$\frac{\text{Knife-edge radius}}{\text{pointer radius}} = \frac{\text{area of free surface of mercury}}{\text{area which the mercury would have if the air bell were not in position}};$$

also the pointer radius is equal to half the length of the air column when of standard value. If the volume of saturated gas is required as with a wet meter a few drops of water are let in through the stop cock. If of dry gas the mercury is left dry.

The balance arm carries a siphon G, the upturned mouth of which describes a path which lies on the circle of curvature of the half-size hyperbola. The siphon's other leg dips in a front annex of a trough shown dotted, and water is supplied to this trough at a rate somewhat in excess of that at which it will be abstracted by the next part of this mechanism to be described. The water then in the trough will always be at the required reciprocal level.

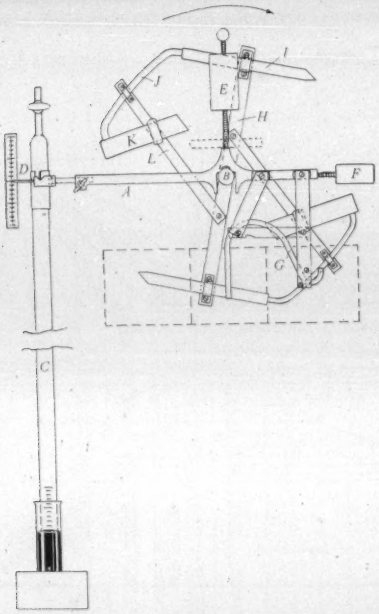

Figure 3.

I should here say that if the mouth of the siphon were left free the water would form a convex dome over it before overflowing, and owing to its surface tension the level of no pressure would be above the dome and the perfection of the geometrical theory would be lost. I have got over this difficulty by springing over the mouth a clip pinching it front and back on a line parallel to the axis. This has the effect of draining water away down to this level, which accordingly is that of the free surface of the water in the trough as required.

It may be interesting to see to what extent the geometrical theory as given approximates to the theoretical requirements. I have accordingly calculated table 1, which needs no explanation except that as I am making 10 in. the unit of my large hyperbola the errors given in inches are errors on 10, not on 1.

Table 1

Gas-volume	Reciprocals (in.)	Siphon levels (in.)	Error in 10 in. (in.)
0·90	10 + 1·1111	10 + 1·1012	−0·0099
0·92	10 + 0·8696	10 + 0·8644	−0·0052
0·94	10 + 0·6383	10 + 0·6361	−0·0022
0·96	10 + 0·4167	10 + 0·4160	−0·0007
0·98	10 + 0·2041	10 + 0·2040	−0·0001
1·00	10 + 0·0000	10 + 0·0000	0·0000
1·02	10 − 0·1961	10 − 0·1960	−0·0001
1·04	10 − 0·3846	10 − 0·3840	−0·0006
1·06	10 − 0·5660	10 − 0·5639	−0·0021
1·08	10 − 0·7407	10 − 0·7356	−0·0051
1·10	10 − 0·9091	10 − 0·8991	−0·0100

From this it will be seen that over the useful range the approximation is good to about $\frac{1}{500}$ in. in 10 in. I should here remark that as the long air tube is carried by knife-edges and not by a band over a concentric arc the sine of the angle of tilt is double the gas-volume ratio, it is not the angle itself; and the difference between the sine and the arc reduces the error which would have been caused by support from an arc to about half its value. You must remember that the contact of a hyperbola with its circle of curvature at its vertex is one of the third order and so for a short distance on either side the separation of the two curves is insensible. Or if you prefer to look at it from the analytical standpoint this is given by the known expression $\frac{1}{6}\frac{d\rho}{ds}\frac{(\delta s)^3}{\rho^2}$, the symbols having their usual meanings. The figures in the table followed simply from the use of a table of sines to find the angles of tilt, followed by an evaluation of the consequent motion of the centre line of the siphon mouth.

Having a satisfactory solution of the first step in the problem—that of obtaining reciprocal water levels—I must now pass on to the second step, how to scoop up from the trough quantities of water which are in these proportions and not only scoop it up but raise it considerably so that the water pump, hitherto a necessity, may disappear.

For the purpose of scooping up water I use a water wheel *H* carrying a pair of similar scooping elements. Each of these consists of a main tube *I*, an adjusting-tube *J*, and a pitcher *K* to lift the water well above the axle and there deliver it in a smooth stream without any splash. These are all secured to a spider frame *HL* carried on an axle running in ball bearings. These elements are so constructed that when the water is at the depth corresponding to standard volume of gas the mouth of the main tube emerges from the water when the adjusting-tube is half immersed, and the two contacts with the water subtend a right angle at the axis. The amount of water so picked up is the standard amount required when the gas-volume is 1·000. If the gas-volume is greater the water-level is lower, and when the mouth of the measuring-tube emerges from the water the adjusting-tube is raised above its former position while the water-level is lower to the same extent, and so there is a double

reduction of the quantity scooped up. In addition to this it will be seen that the adjusting-tube, at least in its standard position, cuts the water at an angle of 45°, and so the change of length of adjusting-tube containing water is $2\sqrt{2}$ times the change of water-level. What then must be the form of curve of the adjusting-tube so that over the whole variation of depth the change of contents shall be in the same reciprocal proportion as the water-depths? It is here that I am able to utilize the variations in the angles between the radii of figure 1. By the properties of the hyperbola the areas of the vertical strip and of the horizontal strip and of the triangle with its vertex at O and terminating in any arc such as AB or AC are all absolutely equal to one another. These triangles are almost exactly equal to the corresponding triangles with their vertices at P, the error here being due to the small curvature telling in opposite directions in the two cases. The areas of vertical elementary strips represent the water required to be scooped up, so the triangular areas with their vertices at P are almost exactly in the right proportion and the arcs of the circle of curvature are exactly in the same proportion as these areas. It is only necessary therefore that the adjusting-tube should be bent to an arc having a radius double that at which its working centre is placed, so that water varying in quantity inversely as the gas-volume may be scooped up. It will be evident that this requires that the balance arm carrying the siphon should turn about an axis absolutely on the same level as that of the water wheel. I make sure of this by using the axle of the water wheel as that on which the ball-bearing reel of the balance arm is mounted.

I have calculated a table of the errors due to the imperfections of the close approximations upon which I have relied in the design. These are not based upon any hyperbolic theory, but starting with the liquid-levels from table 1 and the solutions of many triangles which follow directly from the construction, the actual figures for the calculated water scooped up for the whole range of gas-volumes from 10 per cent below to 10 per cent above standard are given in table 2.

Table 2

Gas-volume	Arc of hyperbola	Same in minutes	Siphon-level, less 10 in.	Proportional error, 10,000ths of total
0·90	+12° 40′ 59″	+760·98	+1·1012	−8·3
0·92	+ 9 56 24	+596·40	+0·8644	−4·9
0·94	+ 7 18 17	+438·28	+0·6361	−2·6
0·96	+ 4 46 19	+286·32	+0·4160	−0·9
0·98	+ 2 20 18	+140·30	+0·2040	0
1·00	0 0 0	0	0	0
1·02	− 2 14 48	−134·80	−0·1960	0
1·04	− 4 24 19	−264·32	−0·3840	+0·8
1·06	− 6 28 47	−388·78	−0·5639	+1·8
1·08	− 8 28 24	−508·40	−0·7356	+3·0
1·10	−10 23 27	−623·45	−0·8991	+5·0

Such a degree of perfection in the geometrical basis on which an instrument can be constructed is more than might have been hoped for. Indeed when I was starting on this quest one of a younger generation observed that if I could get

anywhere near it would be a fluke. Now in consequence of my ecclesiastical upbringing I do not like this word fluke but prefer the expression used by a Bishop on a certain occasion. He said, "a merciful dispensation of Providence". I think that is more appropriate, but whether this dispensation was that there should be

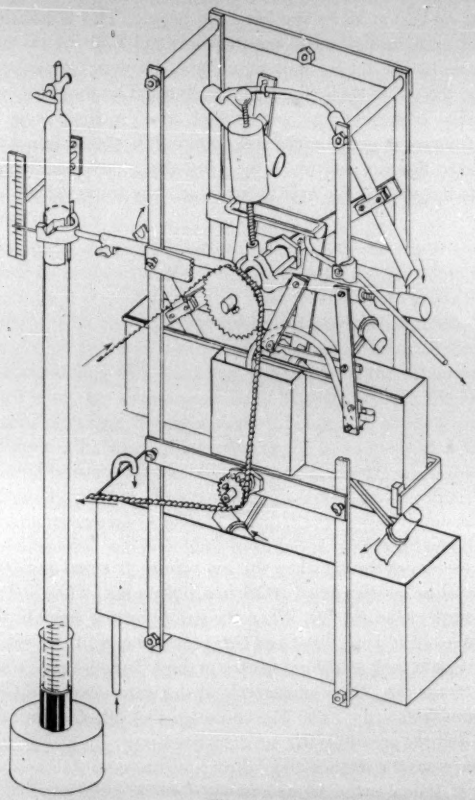

Figure 4.

that half-size hyperbola or that I should have discovered it and all its consequences I do not know. I feel however that I may say in extenuation, "Heaven helps those who help themselves".

It only remains to indicate how water slightly in excess of that scooped up by the water wheel is supplied to the trough in which the water wheel dips. This is very clearly shown in figure 4 which was drawn for me by Prof. C. L. T. Griffith,

using his method of projection which he described at a meeting of the Society of Engineers in November 1932[3].

It will be seen from this that there is a lower main trough which contains water enough to last for months. A lower shaft running in ball bearings carries four thimbles and the two shafts are connected by a sprocket chain and sprocket wheels made at almost no cost at all by the Meccano people. This is not the first time I have used their units in instrument-construction and I am by no means alone in such use. I should like to say how much may be done to assist experimental construction by the use of their admirable products. The thimbles in turning over at the top of their path pour their contents on to an inclined ledge of the upper trough. In this figure the clip on the siphon mouth is shown in position.

A reference to figure 5 will make the geometry of the position more easy to follow. In this figure O is the axis about which the water wheel turns, AB the

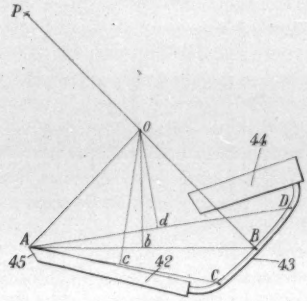

Figure 5.

water-level in the upper trough when the gas-volume is 1·000 and Ob the distance of the water-level below this axis. AOB is a right angle, $PO = OB$, and P is the centre of curvature of the arc CD. When the gas-volume is small or the gas dense, AD is an example of the water-level and Od is the distance of the water-level below the axis. Conversely with a low barometer or high temperature, when the gas is expanded and less dense, AC is an example of the water-level and Oc the distance of the water-level below the axis. The distances Oc, Ob, Od are taken from the previous table and the arcs BC, BD are calculated.

Now passing from the mathematical theory of the water-doling unit to practical considerations of design, manufacture and use, I would point out that all the water-measuring parts of the water wheel are made of triblet-drawn brass tubing of which any amount is to be had all identical in bore. These merely have to be cut to length or bent in a bending machine, put together with the spider frame in a jig and there soldered into a metallic whole. Any number can be made exactly alike and the cost need not much exceed so much a pound for brass. Further, in use there is nothing to wear or alter for there are no internal moving parts. After 100 years of continued service there would be no wear or change. The cost of operating this unit is also

so small that it can hardly be expressed. It may require a gallon or two of distilled water a year to make up for evaporation in the closed cupboard in which it operates. This contrasts with one method in use which pours 300,000 gallons of good water into the drains every year at a cost of about £15, a plan which besides being wasteful is liable to be forbidden at any moment in a year such as the present by the Minister of Drought.

The motor which I have used for this purpose is the larger Everett-Edgcombe motor used in synchronous clocks. This is of ample power to turn the water wheel and the auxiliary shaft with its four thimbles and so to do all the pumping that is necessary for the operation of the machine. I have also taken the sprocket chain round the driving-sprocket of the gas pump which forms the second element to be described in this lecture. Thus the one motor does the whole work of the instrument with an expenditure of current which is far too small to show on the ordinary domestic meter.

I have gone more thoroughly into the theory and scheme of the water-doling unit than I shall do in the case of the next two units, the gas pump and the calorimeter unit, because it seemed to me that from the point of view of this society the hyperbolic theory of its operation should have a particular interest.

Before passing on to these, however, I can give you a better idea of the operations of the water-doling unit than you can get from the actual instrument now working, which is too far away from you to be seen, or from the lantern slides of the parts at rest, as I have the advantage of being able to show you through the skill of Fox Photos a kinematograph view of the instrument, first from a distance at which it can all be seen and then by means of a close-up when the silent teeming of the water from the pitcher, the drip from the siphon and the intermittent outflow from the calorimeter can all be seen in turn.

The gas-doling unit which I have to describe next is a complete break-away from all existing practice. The fact is that in no calorimeter yet made, including my own, is the gas as now often supplied to the consumer ever examined at all. In many cases the gas is contaminated with an impurity and it is only the diluted and adulterated gas which is tested, and then some allowance is made to counteract the bad effect of the diluting material. You may not know it, but in the last few years very great changes have been made by the gas-makers in the perfection of their product. I may mention it as a fact, but it is hardly within the scope of this lecture. First the South Metropolitan Gas Company introduced a dry process whereby they were able to reduce the amount of sulphur present in the gas to an extent hitherto considered impracticable, and recently the Gas Light and Coke Company have introduced a wet process with the same object, a most important advance so far as the consumer is concerned, because it is the acid products of combustion that destroy not only calorimeters but geysers and other appliances in which gas is burnt. But that is not the particular improvement which I wish to dwell upon just now. I wish to draw your attention to the effects of a process introduced a few years ago by W. and C. Holmes Ltd., of Huddersfield, who provide plant for drying the gas so thoroughly that it may not even have a dew point at all.

It then has only a hoar-frost point. It is this dry gas that so often the consumer buys, and it is measured almost universally by the consumer's dry meter. All existing calorimeters pass the gas through a wet meter in which it becomes saturated with water vapour and increases in volume in consequence by something over 1 per cent, and it is the calorific value of this diluted gas that under the requirements of Acts of Parliament prior to 1929 has ever been tested in calorimeters. Even where gas is not artificially dried the gas-maker is prejudiced by the pre-1929 methods, because on the whole the gas received by the consumer is not saturated at 60° F. and the difference, small though it be, is in effect a present to the consumer.

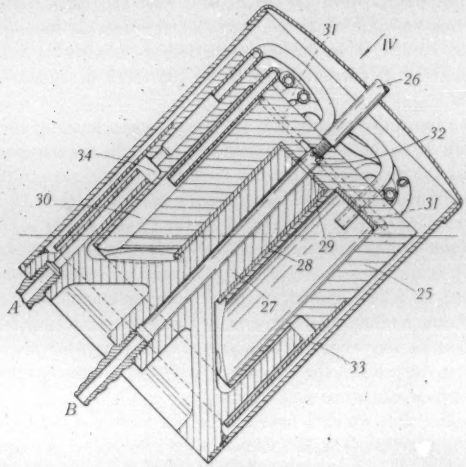

Figure 6.

I had already before the dry gas came into use improved the laboratory wet meter in accuracy out of all knowledge, and I was thus in a position with first-hand experience in meter-design to cope with the new problem. The domestic dry meter has never been made to work with an accuracy such as is essential for our present purpose. After one unsuccessful effort I have succeeded in producing a gas pump driven by external power which so far as I know at present meets all requirements. I designed this after the failure of the first on the 9th February last and it was this lecture looming ahead that made it imperative to find a satisfactory solution. Necessity is the mother of invention most assuredly.

Perhaps the best way to deal with this new invention is simply to show you drawings of the result. Figure 6 is a longitudinal section and figure 7 an end view of the new gas pump and figures 8 and 9 are side and end views on a smaller scale of the levelling-stand which carries it. A cast-iron base 27 carries a cast-iron rotor 25 with a steel tube 28 between for smooth working. The rotor has six

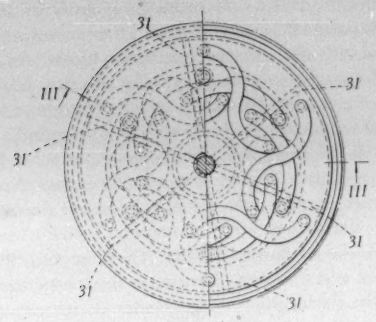

Figure 7.

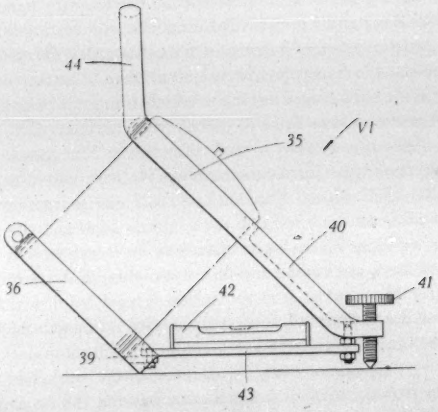

Figure 8.

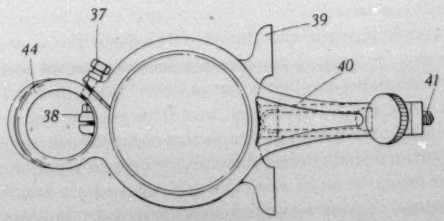

Figure 9.

cylindrical compartments drilled and reamed out truly in all respects, and the interiors of these compartments are connected at the proper times by the steel tubes seen at the upper end with inlet and outlet gas spaces by the immersion or emergence of the twelve tubular passages in mercury. The mercury fills the instrument up to the level line shown cutting diagonally across. The gas enters at A and leaves at B. The rotor is turned by a gear wheel carried on the spindle 26 outside the dust cover. Well, that is all. Nothing could be more simple or, as I have found, more perfect. The delivery of gas resulting from a uniform rate of rotation of the rotor is very nearly uniform, having only a small harmonic variation in each 60° of rotation. Successive sixths of a turn are however exactly equal in this respect. More important still, the gas burns steadily. There is not a flicker as the several valve tubes are sealed and unsealed. I mention this particularly because the few people who have gone thoroughly into gas-meter design are aware how difficult it is to avoid such trouble even with water as the fluid. With mercury I expected greater difficulty but I have found none. I made this instrument in three weeks, the programme having been—one week-end in the country making patterns; the next week Messrs Sugg and Co. provided excellent iron castings; the second week-end I worked up the castings, putting in a 14-hour day from 9 a.m. to 11 p.m. turning cast iron so as to finish the instrument at once. The third week-end cutting the screws within the steel containing-tube which I had not been able to get before, and outside the cast-iron base so as to make a real mercury-tight joint. Then I set it to work and it has run without a hitch ever since. The mercury shows no sign of corrosion or dirt and the turned surfaces on the iron where exposed to the dry gas are only darkened in colour. Should the instrument be used on gas badly fouled with tar fog the rotor can be lifted out at any time and it and the mercury cleaned if necessary, but a proper filter should obviously be interposed in the supply tube. Perhaps I should have mentioned the fact, even though it must be obvious, that the volume of gas doled out at each revolution is $12ar \cot \theta$, where a is the cross-section of any of the cylindrical spaces, r the radius about which their axes are turning and θ the inclination of the axis of rotation. These quantities are from the nature of the design capable of being reproduced in the workshop with a precision approaching 1 in 10,000, and it is my present view that the capacity of the instrument will be determinable more exactly from its dimensions than from trials with holders, bottles, and such devices. Identity of pressure and temperature in such tests is not too easily attained.

Like the water-doling machine this also I believe to be everlasting and it requires no attention or checking when once it has been set up correctly. I should put in a ball-thrust bearing but that is not shown.

The third element is the calorimeter unit. The general principles on which a water-flow calorimeter depends are so simple that it might be thought that the design of such an instrument should offer no difficulty. When, however, the aim is to make a calorimeter free from the faults of all existing calorimeters and that it should be not expensive, but easy to use, accurate beyond prior instruments, and everlasting, it will be evident that the problem cannot be so very simple. For nine years I was

engaged on this, making, trying, altering and remaking, but I was never satisfied until I produced the instrument I have here now. This I believe to be not only better than any which have been used for testing gas companies' gas, but to be ready to take its place with the most perfect apparatus used in research in determining the heats of combustion of the standard pure gases.

The important features are as follows: (1) Very complete jacketing of all the cold-water parts by incoming cold water, and similarly jacketing of the hot-water parts by the hot water leaving the instrument and jacketing of the section in which the water is rising rapidly in temperature by a shield similarly rising in temperature. While insulation might and no doubt would be used it has practically nothing to do and as now working there is no insulation at all other than quiescent air. (2) Complete elimination of all destructive action by the gases and products of combustion, which may be acid and highly corrosive. This is effected by the use of a pyrex-glass open burner, an ordinary-glass chimney, and an ordinary-glass combustion vessel. While ordinary glass works quite well it might be safer to use pyrex glass for the chimney and combustion vessel. I made the one I am using myself by drawing out an Argand chimney and so making a vessel like a short test tube. These are the parts exposed to hot gases. When the greater part of the heat has been removed the gases and liquid products pass over base-metal cooling surfaces, cast brass and German silver, soldered with soft solder. These are protected on the gas side by a layer of Bakelite varnish specially prepared for me by Mr Sallas of the Bakelite Company. I varnished these parts and baked the varnish on, following his instructions with the most scrupulous accuracy. The result is that though I had this running for some months early last year and then left it to soak for a year and this year have again had it running for some months, the condensation liquid is clear water-white, whereas the corresponding liquid from calorimeters as generally used has a bluish tinge when acid, a bright blue colour with ammonia, and when it is treated with ferrocyanide of potash there is a deep chocolate colour. Not only is the condensation liquid when acid not coloured but whether treated with ammonia or ferrocyanide it is still clear water-white when seen through a depth of 15 in. It is for this reason that I put forward the suggestion that the instrument is everlasting. What I cannot tell of course is whether the acid attack will in time damage the bakelite. When cooled the gases and condensed products pass through a tray and tube of ebonite which also resists their action.

Remaining features are of course complete counter-current interchange of heat between the water and the gases and careful proportioning of gas and air for combustion and means for determining any very small want of balance in the amount of sensible heat entering and escaping with the gases, and the highly important effect in the case of dryish air and gas of more water vapour leaving the instrument than enters. This is important on account of its great latent heat, and this in spite of the fact that with gas as supplied burning in air there is a contraction of about $1\frac{1}{2}$ times the volume of the gas. Major Hyde has given me the figure of 5° F. as being approximately the proper excess over inlet-air temperature for there to be a perfect balance in this respect. When we come to determinations of calorific value

much exceeding 1 in 1000 in accuracy, then the question of definition becomes important, but that I have on the present occasion no intention of discussing.

With these general observations there is little more to say than to refer to figure 10, which is a vertical section of the instrument, while figure 11 is a vertical

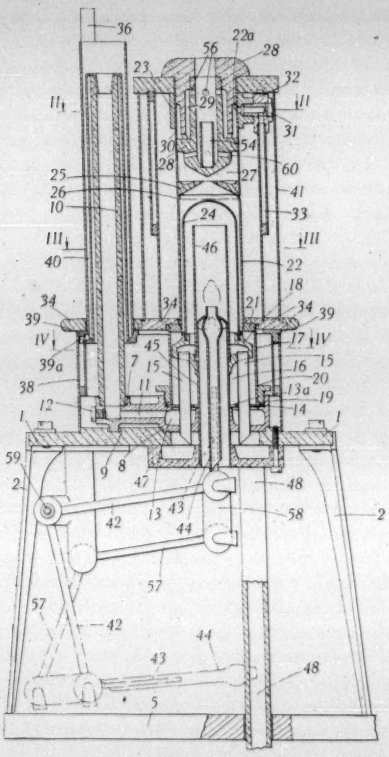

Figure 10.

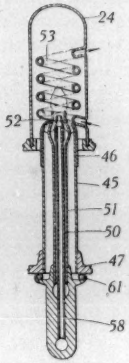

Figure 11.

section of an alternative element specially designed for work of the highest accuracy on the heats of combustion of the standard gases.

The cold water enters at 36, circulates through the cold-water jackets 38 and 40, and passes through the cold-water thermometer pocket 10. It then passes twice past the German silver cooling tubes 15, up round the combustion vessel 24 and the hot thermometer pocket 54, then through the hot-water jacket 33, and out by a tube at the back which cannot be seen in the figure. The gas is brought in to the

parallel motion burner support at the swivel 59. The pyrex-glass burner tube 44 is pushed up against claws to locate it, so that the air-gas flame is central and always in the same position. 46 and 24 are the chimney and combustion vessel each made of ordinary or pyrex glass. The hot gases descend through the glass-walled annular space, then through the tubes 15, and out through the dish 47 and down tube 48. This latter is provided with exit thimbles of various sizes so that the flow of gases may be restricted to that which gives the greatest rise of temperature. Actually there is no observable difference for a small variation until the air becomes insufficient, when the reduced rise is manifest and the smell of the exit gases becomes pronounced. In the laboratory the chemical analysis of the products of combustion gives all desired information as to air-gas ratio, but the thimble plan is simpler and is more adapted to routine operations. Provision is made for ascertaining the temperature of the exit gases at the top of the tube 48 and of the inlet air alongside, which is also that of the gas.

With the calorimeter as I have made it the exit gases are only $1\frac{1}{2}^\circ$ C. above the inlet water. An increase in the lengths of the tubes 15 would reduce this very slight loss of heat, but it is better to allow for this rather than eliminate it by undue lengthening of the cooling tubes.

It may be interesting to observe that the hot thermometer settles down to its steady value in 15 min. from that of starting up all cold, and that though the water supply is intermittent with a half-minute period the hot-water thermometer shows no fluctuation of as much as $\frac{1}{100}^\circ$ C. even with a temperature-rise of 20° C. These are both valuable results which I have not seen approached in any other water-flow instrument. The hot exit water passes on its way to the cooling coils below, from which it returns by a tube shown to the left of the lower tank in figure 4.

If the temperatures are accurately determined and the deliveries of the water and gas are verified the limits of accuracy are settled by the limitations of the thermometers for measuring the temperature-rise of the water, whether these are mercurial or electric, and this limitation applies to all calorimetry. For the most accurate determination of the heat of combustion of standard gases it would be advantageous not to have so great a proportion of nitrogen in the exit gases, for this adds to the difficulty of complete cooling in the heat-interchanger as well as to the determination of the heat balance between incoming and outgoing gases. For this reason I have provided for this special purpose the variation in design of the burner and combustion chamber shown in figure 11. In this 58 is the link of the parallel motion, but the gas to be burned is brought in by the lower swivel pipe 57 and oxygen or other gas according to the reaction to be examined is brought in by the upper swivel pipe 42. The burner tip 52 may be made of fused silica and the oxygen or other gas tube 51 of pyrex glass or silica. The combustion vessel 24 is now provided with a water-cooled worm, so that the gases from the intensely hot flame may be cooled in passing up and so strike the top of the dome without harm. This part might be made of transparent fused silica for safety, but I have found that pyrex glass is not damaged and it is very pretty to see the formation of steam in the worm. This being lighter than water hurries the circulation. The top

of the link 58 carries a closing dish with an umbrella ring 61 to make a sufficiently gas-tight joint.

It will be evident from an inspection of the drawing, figure 10, that the calorimeter unit has been designed to take a mercurial thermometer, or if required the "bulbs" of a differential electrical thermometer which need occupy but little more space than is required by a mercury thermometer. For this reason I am unable to use the large vessels containing amyl alcohol which actuate the recording pen of my present recording calorimeter. While these work perfectly when the soldered joints do not leak they have two disadvantages which I wish to avoid. The first is the great heat capacity. The second and more serious disadvantage is the extended surface from which transfer of heat to the outer world may take place, or the increased difficulty of insulation. I have therefore decided to adopt the differential electrical thermometer with recording mechanism. Several of these already exist and I have not in consequence undertaken the design and construction of a new one. I have ideas on this subject but it seems best in the first instance to use what is already available.

In this lecture I have omitted all description of details of necessary adjuncts, which, being more or less commonplace and obviously essential to the use of the instrument, would detract from the interest which I hope will be found in the originality of the three units which I have described.

Anyone who would accept the honour of being the Guthrie lecturer would wish that he had something new and valuable to describe, but in my case seeing how much I owe to the late Prof. Guthrie, and to the terms in which at the beginning of this lecture I have interpreted the soul of Guthrie, more than ever is it essential that I should have something which with my recollection of him I know would have met with his approval; I hope I have succeeded.

Note. Owing to the official character of my work in designing these units with a view to their being adopted by the Gas Referees, of whom I am one, for testing the gas supplied to the public it has been necessary to make a formal agreement with a manufacturer. Official patents had been obtained by a Secretary of the Board of Trade and myself as inventor and a formal licence had to be granted to a manufacturer. Messrs Casella and Company Limited were selected. I have kept back the publication of this lecture until I could give the story complete up to this stage, and now (February 1936) I have received the agreement signed by a Secretary of the Board of Trade, and Messrs Casella are able to start on the making of the first unit.

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THE CONSTANCY OF THE VELOCITY OF SOUND AT SONIC FREQUENCIES

By F. A. WALCH, Ph.D.

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Read October 9, 1936

ABSTRACT. A method of investigating whether there is any dispersion of sound waves in air at sonic frequency is described. It consists in comparing the wave-form of a complex sound at different distances from the source. A technique for making the necessary collodion diaphragms has been worked out, and a simple but effective drum camera constructed. A controllable wave-form is provided by two oscillators, one tuned to a fundamental and the other to a harmonic, locked into synchronism by close coupling. Frequencies from 250 to 1000 c./sec. have been investigated. Velocities have been proved constant for the lower frequencies to within 1 in 500 and for the higher frequencies to within 1 in 1000.

§ 1. INTRODUCTION

The constancy of the velocity of sound with frequency at audio frequencies always seems to be taken as an accepted fact. It appears, however, that no accurate and systematic investigation over the whole audio range has ever been undertaken by any one observer. Diverse methods in the open air and many varieties of tube methods give results which agree fairly well with one another, but of the direct methods those giving consistent results have been undertaken either at one particular frequency or over a very limited range of frequencies. It has never been directly proved that the velocity of sound, say between frequencies of 200 and 1200 c./sec., does not vary by more than 1 in 1000. Various qualitative arguments are advanced in support of the constancy of the velocity. Of these the most common is that when an observer listens to an orchestra playing at a distance he hears the piece performed in correct time just as it is being played. If sound of different frequencies travelled at different rates it is obvious that the time of the piece would be disturbed, chords would be broken into their constituent notes, and in an extreme case even the sequence of the notes might be altered.

On considering this argument quantitatively, it is found that such constancy as it establishes is useless as far as scientific measurement is concerned. It is well known that there is a phenomenon, persistence of hearing, analogous to persistence of vision. Thus, two sounds separated by a time interval of less than $\frac{1}{10}$ sec. are not heard as two separate sounds. Applying this to the above argument, we see that if we are to be able to detect a disturbance in the music due to sounds of different frequencies travelling with different velocities, then one note must gain upon the other to such an extent that they arrive at the ear of the observer with a time displacement from the original of more than $\frac{1}{10}$ sec. If the velocity of sound is taken to be 300 m./sec., it is easily shown that in order to detect a change even

as large as 1 per cent, i.e. 3·3 m./sec., one must be about 3000 m., i.e. 2 miles, from the source. At this distance not even the loudest of brass bands would be heard with sufficient distinctness to enable one to make observations.

The experiments to be described were undertaken with the object of investigating the constancy of the velocity of sound by a direct method at frequencies covering the audio range. The phenomenon described above was applied quantitatively. The wave-forms of complex sounds, i.e. of sounds containing a number of different frequencies, were photographically recorded at different distances from the source and analysed. If one harmonic of the complex wave has a velocity differing from that of the others, then there will be a change of wave-form. The change in phase-difference between the two harmonics with distance gives a measure of the velocity-difference. The method, therefore, only measures velocity-differences, but small differences cause quite large phase-changes and the method is independent of such factors as temperature and humidity, since it in no way depends on the actual value of the velocity.

Another great advantage is that the fidelity of the recording apparatus, i.e. the agreement between the actual air-pressure variations received by the recorder and the wave-form recorded on the photographic film, does not need to be of the high order that is required, for instance, in speech-recording of the type undertaken by Crandall and Sacia[1], whose experimental efforts were mainly directed towards the attainment of this high fidelity. In other words, resonance effects of various kinds, in loud-speaker, horn and diaphragm, which are always present in all types of recording instruments and are usually one of the main sources of difficulty, are not, in this case, of major importance. Only differences between very similar wave-forms are required and not the wave-forms themselves. The effect of resonances in the present work was to reduce the accuracy with which the wave-form of a trace could be predicted from an examination of the electrical output of the oscillator with the cathode-ray oscillograph.

Since high fidelity was not essential it was possible to use an apparatus which is simple compared with the calibrated condenser microphone and high-fidelity multi-stage amplifier usually necessary for sound-recording.

The detecting apparatus consisted of a thin collodion membrane on which is deposited a gold, silver or platinum mirror so thin that its mass does not affect the vibration of the membrane. By means of a beam of light reflected from this mirror a photographic trace is obtained showing its motion. Before the apparatus is described in detail, however, it will be interesting to get some idea of the value of the phase-variation which it is hoped to measure.

A sound-wave falling upon the membrane can be represented by

$$y = A \cos \omega (t - x/c),$$

x being the distance from the point where the displacement is $y = A \cos \omega t$. For simplicity consider a complex wave consisting of a fundamental and one harmonic only:

$$y_0 = A_1 \cos (\omega t + \epsilon_1) + A_n \cos (n\omega t + \epsilon_n),$$

where y_0 is the displacement at $x=0$. Now suppose the distance from source to membrane be increased by an amount x. Then we have

$$y_x = A_1' \cos\left(\omega t + \epsilon_1 - \frac{\omega x}{c_1}\right) + A_n' \cos\left(n\omega t + \epsilon_n - \frac{n\omega x}{c_n}\right),$$

where c_1 and c_n are the velocities of the 1st and nth harmonics of frequency $\omega/2\pi$ and $n\omega/2\pi$ respectively. Then the phase-change between the 1st and nth harmonics due to the difference between their velocities is obtained from

$$y_0 = A_1 \cos(\omega t + \epsilon_1) + A_n \cos(n\omega t + \epsilon_n),$$

$$y_x = A_1' \cos\left(\omega t + \epsilon_1 - \frac{\omega x}{c_1}\right) + A_n' \cos\left(n\omega t + \epsilon_n - \frac{n\omega x}{c_n}\right),$$

whereas if the nth harmonic had the same phase-velocity as the fundamental we should have

$$y_x' = A_1' \cos\left(\omega t + \epsilon_1 - \frac{\omega x}{c_1}\right) + A_n' \cos\left(n\omega t + \epsilon_n - \frac{n\omega x}{c_n}\right),$$

$$\text{Phase-change} = n\omega x\left(\frac{1}{c_1} - \frac{1}{c_n}\right) \text{ radians},$$

$$= 2\pi n f x\left(\frac{1}{c_1} - \frac{1}{c_n}\right) \text{ radians},$$

since $\omega = 2\pi f$, where f is the frequency of the fundamental

$$= 360 n f x\left(\frac{1}{c_1} - \frac{1}{c_n}\right) \text{ degrees},$$

and is positive if $c_n > c_1$.

Suppose we wish to detect a velocity-difference of 1 in 1000, so that

$$c_n = \frac{1001 c_1}{1000},$$

$$\text{Phase-change} = 360 n f x\left(\frac{1}{c_1} - \frac{1000}{1001 c_1}\right)$$

$$= \frac{360 n f x^\circ}{1001 c_1},$$

$$= 0{\cdot}36\,\frac{n f x^\circ}{c_1} \text{ approximately.}$$

As the phase-changes are themselves small, the approximation gives negligible error.

As an example consider a typical wave-form made up, say, of frequency 400 and its 3rd harmonic of frequency 1200, the distance x being 300 cm. Substituting in the above formula we get

$$\text{Phase-change} = \frac{0{\cdot}36 \times 3 \times 400 \times 300}{33{,}000},$$

$$= 4^\circ \text{ approximately.}$$

Thus, under these conditions, if we can measure phase-changes to within 4°, we can detect velocity-changes of 1 in 1000 between the frequencies 400 and 1200. The accuracy with which the phase-changes can be measured will be determined by (1) the accuracy with which measurements can be made on the photographs, and (2) the greatest distance x for which measurements are possible. These two factors are interconnected, in that if x is to be large, then the magnification of the system must be made large and consequently definition suffers. The way in which these two factors have been combined to give the most favourable conditions will be discussed in the description of the apparatus.

§ 2. THE APPARATUS

The detecting apparatus as first set up is shown diagrammatically in figure 1. It consisted essentially of a box B specially designed to carry the sound-sensitive collodion membrane D, upon which was deposited a gold mirror. Light from a

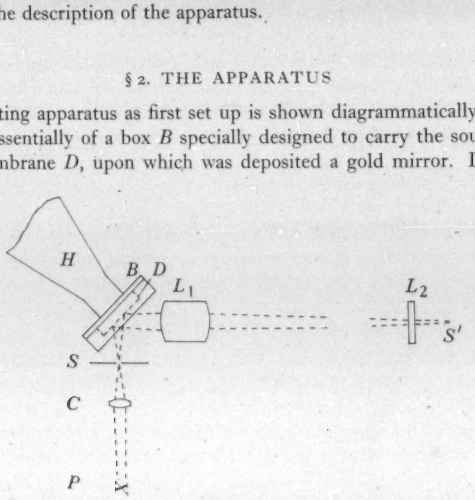


Figure 1.

Pointolite source P passed through a condensing-lens C and a slit S placed close to it, C forming an image of the Pointolite bead on the membrane mirror, which reflected the light through 90°. A projection lens L_1 formed an image of the slit S on the photographic film. A cylindrical lens L_2 condensed the image to a fine tracing point at S'. Use was made of a spool-and-sprocket camera of standard design, capable of a maximum film-speed of about 3 m./sec.

Traces obtained with this preliminary apparatus showed that the optical definition and brightness of the tracing point were insufficient for accurate analysis. The wave-length of the traces was too short, so that a higher film-speed was necessary. An increase in the acoustical sensitivity of the apparatus also was needed to lessen the volume of sound necessary to produce a sufficient amplitude. This would reduce the possibility of interaction between source and receiver, which was the probable cause of some of the large changes in wave-form with distance obtained with the preliminary apparatus.

§ 3. THE OPTICAL SYSTEM

The original optical system was considerably modified. This system, which is very popular in talking-picture sound-recording[2], gives good definition, but the amount of light concentrated into the spot is small since only a tiny fraction of the total light emitted by the source is used; the ratio of the actual area of the slit to the area of the whole sphere receiving light is extremely small.

The system eventually adopted is shown in figure 2. Light from the arc S was concentrated by means of a condensing system C upon a fine wire O, 0·002 in. in diameter, which formed the object. S was not focused upon O, for this gave rise to unequal illumination of the final image, and the divergence of the rays after leaving O rendered difficult the formation of a small intense spot on the diaphragm mirror M. Actually the arc crater was focused on to the mirror, or, what was practically the same thing, on to the diaphragm D which was used to exclude the extreme

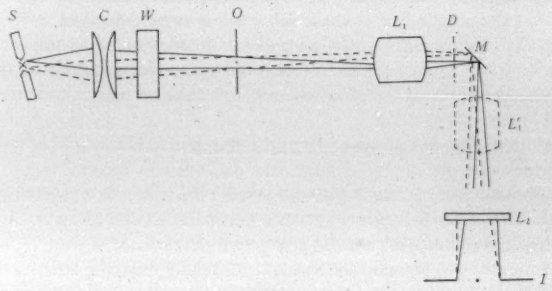


Figure 2.

rays. This was easily visible, and was therefore used for focusing-adjustments in preference to M, which was not easily visible. A water cell W was included between C and O to prevent undue heating of the membrane at M. The image of O was projected in the earlier experiments by a 20-cm. Leitz projection lens at L_1'. It was later found advantageous to have the projection lens at L_1. The image of the fine wire O was formed at I and condensed down on to the camera slit by the cylindrical lens L_2.

The use of a fine wire as object was dictated by the limitations imposed by the use of a slit. The fine wire has the fundamental advantage that the effect of diffraction is to narrow instead of spread the image. It is also easier to obtain a small spot on the mirror M if a fine wire is used as object. Platinum wires of diameters 0·0005–0·004 in. were tried; a diameter of 0·002 in. was found to be most satisfactory. This was stretched as tightly as possible across a washer of internal diameter $\frac{1}{4}$ in. and the ends were fixed with two small dabs of sealing wax.

By shifting the projection lens from L_1' to L_1, thereby using the whole optical arm MI, the displacement of the image at I for an angular deflection θ of the

mirror M was increased from 150θ to 360θ, while the actual size of the image was only increased in the ratio 2·7 : 3·5. To keep the latter ratio as small as possible, L_1 was placed as close as possible to M.

It is essential for the formation of a well-defined spot that the object wire should be straight and vertical. Deviations from either of these conditions are accentuated when the light is focused down with the cylindrical lens.

§ 4. THE PREPARATION OF COLLODION MEMBRANES

It was realized at an early stage that with the original apparatus the intensity of sound necessary to give a reasonable amplitude was much too great. Apart from the general unpleasantness of working with such high intensities, it was highly probable that interaction was taking place between the source and the receiver. One way in which it was possible to increase the sensitivity of the apparatus was to employ a larger and less tightly stretched receiving-diaphragm. The technique developed for the preparation of these films will now be described.

The method employed for preparing flexible collodion films followed closely that of Dewhurst[3]. Since the films had to be sputtered, a number of breakages was to be expected. It was therefore essential to be able to make a new film without much preliminary preparation.

The solution used was prepared from the standard solution sold by Griffin and Tatlock, which consists of 3 g. of guncotton dissolved in 100 cm.³ of 1 : 1 mixture of ether and methylated spirit. 3 parts of ether were added to 2 parts of the above solution and to this was added 1 part of a 2 per cent solution of castor oil in ether. This solution gave films showing red and green interference colours by reflection, clear and brilliant, and of sufficient strength to stand sputtering without wrinkling or going slack.

The mercury on which the films are to be spread must be very clean and the surface must be free from dust. It is twice passed through dilute nitric acid, twice through distilled water, and is then distilled *in vacuo*. Difficulties due to particles of dust, etc. falling on to the surface are greatly lessened by the use of a dust-free room which exists in the department, designed and furnished specially to reduce the amount of dust in the air to a minimum. The mercury is contained in a shallow dissecting-dish about 15 cm. in diameter and about 1·5 cm. deep. This can be covered by a similar dish of slightly larger diameter to protect the film while this is being dried. Several preliminary films are now formed over the whole surface, allowed to dry, and stripped off. This is necessary so that the collodion may wet the surface; wetting is shown by rapid even spreading in approximately circular shape. When this condition obtains, a few cm.³ of the prepared solution are poured on to the mercury in sufficient quantity to form a film of the required diameter. The solution spreads rapidly at first, then more slowly, and finally starts to contract. The rate of contraction increases until wrinkles begin to appear at the edges of the film, It was found that this was the best time to remove it. The steel ring, turned from Brown and Sharpe's Ground Stock $\frac{3}{16}$ in. thick, $2\frac{1}{2}$ in. in internal and $3\frac{1}{2}$ in.

in external diameter, on which the film is to be carried is prepared by coating it thinly by means of a small brush with a dilute solution (5 to 10 per cent) of Canada balsam in ether. The ring is made to adhere by placing it on the film just before it dries. The excess film round the edges of the ring is removed with a fine needle. The removal of the film from the mercury surface is rather a tricky operation. If, however, the surface is really clean, then, by careful manipulation and a combination of a lifting and sliding motion, films up to $3\frac{1}{2}$ in. in diameter can be removed straight away from the mercury surface. When the film is removed it is found to be loosely stretched, but tightens up as the underside of the film dries.

A milky appearance due to dampness can be removed by gentle heating. The heating must not be too prolonged or too intense since it has a tightening effect. A film so tightened, if left for several hours, becomes much slacker than it was before being heated. The films have to stand considerable heating during the process of sputtering. It is, therefore, advisable to keep them as taut as possible.

The use of ground stock for the rings ensured that they were accurately flat. The size chosen is the largest convenient size for which the percentage of breakages is small. Moreover, sizes larger than this may be comparable with the wave-length of some of the higher harmonics, in which case the pressure due to the incident sound-wave may not be uniform over the film.

§ 5. SPUTTERING ON TO COLLODION FILMS

The apparatus and method of sputtering were similar to those used by Andrade and Martindale. For further information reference should be made to their paper[4].

The apparatus was as described by them, except that the small central disc was replaced by a gold-plated diaphragm, of diameter 3 in., fastened to the cathode by small aluminium clips. The uniformity of deposition necessary to obtain a good mirror did not require a guard-ring.

The Cenco Hyvac pump is connected direct to the jar through wide-bore tubing. A side branch contains a needle-valve leak to let air in slowly when required so as not to burst the collodion film with a sudden rush of air. The absence of traps and the like enormously increases the rate of evacuation, and any oil vapour which may diffuse over does not seem to have any appreciable effect on the rate of sputtering.

The anode is covered by a glass disc upon which is placed the film to be sputtered. The interposition of the disc insulated the film from the anode and there was no tendency for the discharge to pierce the film in order to take the shortest route to the anode. The glass disc does not materially affect the rate of deposition. The process is in many ways analogous to one of evaporation from the cathode and condensation on the cooler parts of the apparatus. This is well shown by the deposit on the sides of the jar, the base plate, and, to a smaller extent, on the back of the cathode.

The circuit used consists of an induction coil working off the 200-volt mains, the primary current being interrupted by means of a mercury break with two large

condensers in parallel. The secondary is connected to the sputterer, and the current measured by a milliammeter of rectifier type. The voltage is estimated by means of another a.-c. milliammeter and a 1·5-megohm resistance, the two being connected in parallel across the sputterer electrodes.

The conditions under which sputtering was carried out were approximately as follows: electrode-distance, 3 cm.; pressure, 0·01 mm.; r.m.s. current, 25 mA.; r.m.s. voltage, 1000 V.; dark space, 1·5–2 cm. In general, on switching on, the voltage drops rapidly at first to a constant value, remains steady for some time and then, if the apparatus is working properly, rises steadily to a constant maximum, the current meanwhile decreasing to a minimum.

Attempts were made at first to sputter a small gold mirror about 0·7 cm. in diameter on the diaphragm. The film was covered by a mica mask containing a hole of the required diameter. On exposing the film to the discharge for a sufficient time to obtain a good mirror, however, the film round the edges of the sputtered area developed a series of small wrinkles radiating from the mirror. It was not found possible to remove these wrinkles, which were probably due to heat radiation from the hot cathode. After 15 minutes' sputtering this was too hot to touch.

To overcome these wrinkling effects the films were sputtered all over so that the final tension would be uniform. The films were made as taut as possible to begin with. The actual sputtering was carried out intermittently, intervals being allowed for the apparatus to cool down. Periods of 10 min. for sputtering and cooling were found to be satisfactory, and the total time to form a mirror was then about 2 hours. The tension of the films was reduced by sputtering, but they still remained sufficiently taut to be used as membranes.

During these experiments it was observed how similar this process is to evaporation and condensation and therefore what an important part the temperature of the electrodes plays. This temperature factor seems to be neglected entirely in the various empirical formulae put forward to give the rate of deposition in terms of discharge constants—current, voltage, pressure, length of dark space. Most experimenters fix the anode temperature by water cooling, but the temperature of the cathode and its effect on the rate of sputtering has been entirely neglected. It was observed in the present experiments that variations in current and voltage had a marked effect on cathode-temperature. It seems likely that some of the complicated effects of variation of current and voltage on the rate of sputtering may be explained in terms of cathode temperature.

§ 6. EXPONENTIAL HORN

To fix these membranes in the apparatus the original diaphragm-holder was removed and the steel ring held in two small brass clamps. These also held a tube of the same diameter as the membrane for connexion to the horn.

The horn was exponential, of length 44 cm., its mouth being 48 cm. in diameter. By measuring the diameter of the horn at various distances from the throat a value

for m was obtained in the formula $S = S_0 e^{mx}$. Actually $m = 0{\cdot}12$, giving a cut-off frequency of approximately 300 c./sec. and horn resonances appreciably below 430 c./sec. As has been explained previously, resonance effects are not of fundamental importance. Experimentally it was found that response did not fall off appreciably till a frequency of 220 was reached, probably due to the increased diaphragm response in this region (diaphragm resonance 80 c./sec.).

The speaker employed was an experimental type kindly lent by Electrical and Musical Industries. It consisted of a large, thin, stretched aluminium diaphragm of diameter 38 cm. rigidly clamped between two steel rings. A small speech coil was eccentrically mounted on the diaphragm and moved between the poles of a mains energized electromagnet. The speaker was capable of handling an enormous range of volume without appreciable amplitude distortion.

§ 7. THE CONSTRUCTION OF A HIGH-SPEED DRUM CAMERA

To make possible a higher film-speed than the 3 m./sec. obtainable with the original spool-and-sprocket camera a drum camera was built to hold two $4\frac{1}{2}$-ft. lengths of film and capable of a maximum film-speed of 50 ft./sec. Actual photographs were taken at speeds up to 32 ft./sec. The traces for analysis were obtained at lower speeds owing to the improved definition thereby obtained.

The camera, which fulfilled many of the purposes of an expensive high-speed camera, was of an extremely simple design due to Prof. Andrade. The total cost in all was not more than £5.

The drum consisted of a standard belt pulley supplied by the Skefco Ball Bearing Co., and had a diameter of 18 in. and a rim-width of $4\frac{1}{2}$ in. It was mounted on a shaft supported by standards and self-aligning ball bearings supplied by the same company. These were mounted upon a bench which could be wheeled into the dark room for loading and unloading.

A light-tight box surrounded the drum and standards. The front of the box carried two slits $\frac{1}{10}$ mm. wide and 4 cm. long, made from razor blades, the outside ends of the slits being opposite the outside edges of the drum. For loading and unloading there was a door 6 in. wide at the back of the box, fastening tightly down on a seating of velvet.

The drum is driven by a small electric motor carrying a 4-in. pulley driving on to a 12-in. pulley on the drum shaft. With this arrangement the motor is self-starting and attains a speed of 900 r.p.m. in about 2 min.

The fixing of the film to the drum presented some difficulty. Various methods were tried, but were cumbersome for use in total darkness and did not hold the film tight and flat. Small pinches of soft red wax were tried at each corner of the film and this method was found to be satisfactory. The film was held tight and flat on the drum and the camera could be easily and quickly loaded. The film used was specially prepared by Messrs Ilford, to whom my best thanks are due, and consisted of a special non-perforated film base coated with their hypersensitive panchromatic emulsion.

In order that the drum should only be exposed for one complete revolution it was necessary to calibrate the shutter, which was of ordinary iris type with time exposures marked $\frac{1}{2}$, $\frac{1}{5}$, $\frac{1}{10}$, etc. The calibration was easily made by measuring the length of film exposed at a known drum-speed. This gave the results shown in table 1.

Table 1

Indicated time (sec.)	Actual time (sec.)
0·500	0·820
0·200	0·330
0·100	0·165
0·085	0·133
0·070	0·097
0·055	0·075
0·040	0·064

This covers a range of drum-speeds from $1\frac{1}{4}$ to 16 r.p.s., intermediate speeds being assumed to follow a linear law.

Some traces with large amplitude and high film-speed are shown in figures 4 *a* and 4 *b*. These were taken with a film-speed of 30 ft./sec. They show how, with large amplitude, the presence of an harmonic of suitable frequency may excite a higher mode of vibration in the membrane which is superimposed on the main vibration. This is indicated by the curious doublings shown in the traces.

§ 8. PRODUCTION OF A CONTROLLABLE WAVE-FORM

What was desired was the ability to add to a fundamental sine wave the desired harmonic in any required proportions. After some preliminary experiments with other methods, it was found that exactly what was required could be obtained by coupling together two audio-frequency oscillators, one tuned to the fundamental and one to the harmonic, provided that the coupling was sufficiently close for synchronism to take place.

It is well known that vacuum-tube oscillators have an inherent tendency to synchronize with any oscillation of approximately their own frequency which may be present. Two factors influence the frequency-difference at which synchronism occurs—the strength of the injected current and the frequency-stability of the oscillator.

This phenomenon of frequency synchronization also occurs to a somewhat less degree between circuits tuned to frequencies bearing integral ratios to one another. It was this property which was utilized. For this purpose use was made of two oscillators. The schematic arrangement is shown in figure 3 *a*. A fundamental was supplied from a Sullivan oscillator which, for convenience, will be referred to as *oscillator A*. It gave a note of very pure wave-form and was of high frequency-stability. Oscillations from oscillator *A* were injected at a suitable point into another oscillator, of lower frequency-stability than oscillator *A*, and tuned to the desired harmonic. This latter oscillator we shall refer to as *oscillator B*.

It was necessary to find a suitable point for the feed-in to oscillator *B*. The grid bias of *B* is connected to the tuned circuit of the oscillating valve and thence to the grids of the amplifiers, figure 3 *b*. The desired effect was obtained by feeding-in oscillations at *A*, i.e. between the grid terminal and the negative of the bias battery. This caused synchronization of the oscillations in the tuned circuit of *B* and the combination was passed on to the amplifying system. The output from oscillator *A* was controlled by a 50,000-Ω. potentiometer *I*.

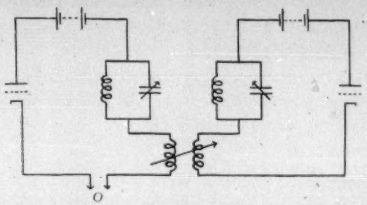


Figure 3 *a*.

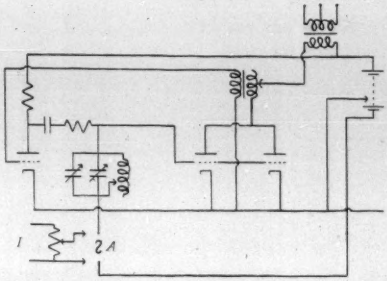


Figure 3 *b*.

The two oscillators were tuned as nearly as possible to, say, the fundamental and the 2nd harmonic, and switched on. In general, beats were heard in the hum of the output transformer and these became gradually slower as the volume-control on oscillator *A* was increased, until at a certain point the beats ceased and a uniform note was obtained showing that oscillator *B* had been pulled into synchronism. As far as was practicable, traces were used containing approximately equal proportions of fundamental and harmonic.

§ 9. METHOD OF TESTING CONSTANCY OF VELOCITY

The oscillators were adjusted to be in synchronism and to give a steady wave-form of the required type. The film-speed used was about 16 ft./sec.

A record of the wave-form at two different distances from the source was required for each frequency. The maximum convenient distance was about 325 cm.

and the minimum 75 cm., giving a distance change of 250 cm. Traces obtained very close to the receiver were inclined to be unstable and to show varying amounts of high harmonics.

If the volume control at the two distances were kept the same, then it was found that the range of amplitude obtained was too large for adequate measurement. To avoid this, the volume of sound was adjusted when the distance was varied so as to make the amplitude recorded on the film the same at both distances. Then, a suitable constant distance having been chosen, the variation with volume over the above range was investigated.

Thus for each frequency investigated we obtain four traces, which we have to analyse so as to obtain their phase relations. We find that measurements of the best traces can be repeated to 0·5 per cent. It is safe to say that the general error in measurement will be of the order of 1 per cent.

We have two functions

$$f_1(t) = a_0 + a_1 \cos \omega t + a_2 \cos 2\omega t + \ldots\ldots + b_1 \sin \omega t + b_2 \sin 2\omega t + \ldots\ldots,$$
$$f_2(t) = a_0' + a_1' \cos \omega t + \ldots\ldots\ldots\ldots + b_1' \sin \omega t + \ldots\ldots,$$

which represent the two traces on the film.

We measure 2ρ ordinates per period A_1, A_2, ... $A_{2\rho}$ and A_1', A_2', ... $A_{2\rho}'$, and hence deduce two functions

$$\phi_1(t) = \alpha_0 + \alpha_1 \cos \omega t + \alpha_2 \cos 2\omega t + \ldots\ldots + \beta_1 \sin \omega t + \beta_2 \sin 2\omega t + \ldots\ldots,$$
$$\phi_2(t) = \alpha_0' + \alpha_1' \cos \omega t + \ldots\ldots\ldots\ldots + \beta_1' \sin \omega t + \ldots\ldots,$$

which pass through the measured points. Since A_1, A_1', etc. are only measured to 1 per cent, measurements of the values of a_n, b_n cannot claim an accuracy greater than 1 per cent.

But another source of error arises in that although $\phi_1(t)$ and $\phi_2(t)$ pass through the given points we have no knowledge as to their behaviour between those points. In other words the αs and βs are determined by a finite summation whereas the true as and bs are integrals.

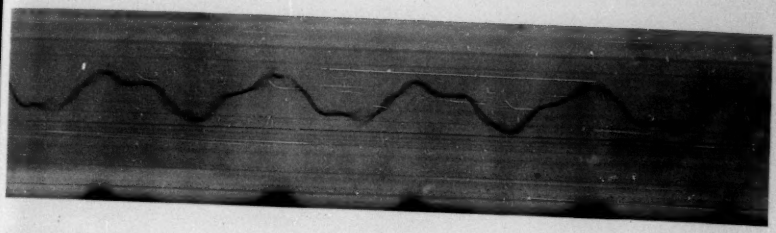
The deviation of the αs and βs found by analysis from the true Fourier constants is given by

$$\alpha_1 = a_1 + a_{2\rho-1} + a_{2\rho+1} + a_{4\rho-1} + a_{4\rho+1} \ldots\ldots,$$
$$\alpha_2 = a_2 + a_{2\rho-2} + a_{2\rho+2} \ldots\ldots,$$
$$\vdots \qquad \vdots$$
$$\alpha_n = a_n + a_{2\rho-n} + a_{2\rho+n} \ldots\ldots.$$

Similarly

$$\beta_1 = b_1 - b_{2\rho-1} + b_{2\rho+1} \ldots\ldots,$$
$$\vdots \qquad \vdots$$
$$\beta_n = b_n - b_{2\rho-n} + b_{2\rho+n} \ldots\ldots.$$

In the present work the amount of high harmonic is small since the wave is an addition of two good sine waves. It will be shown that the amplitude of the 21st harmonic is less than 0·05 per cent of the fundamental amplitude. We can therefore say that the αs and βs will not differ from the true as and bs by more than 1·5 per cent.



(*a*)

(*b*)

Figure 4.

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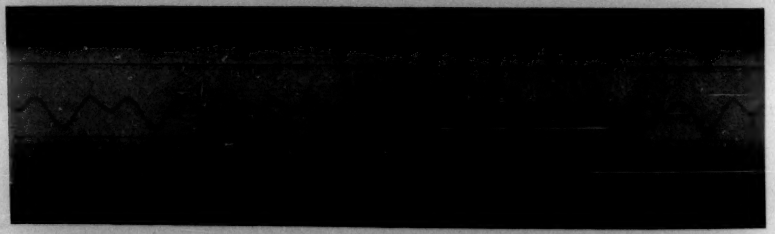
(*a*)

(*b*)



(*c*)

(*d*)

Figure 5.

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It is easy to show that knowing the αs and βs to 1·5 per cent then we also know the tangents of the phase angles, i.e. β/α, to 1·5 per cent and so can detect a difference of 1° in the phase angle θ for all values of θ.

The required amplitudes are calculated from

$$\sum_{q=0}^{2p-1} A_q \cos\frac{qn\pi}{p} = p\{a_n + a_{2p-n} + a_{2p+n} \ldots\ldots\}$$

and

$$\sum_{q=0}^{2p-1} A_q \sin\frac{qn\pi}{p} = p\{b_n - b_{2p-n} + b_{2p+n} \ldots\ldots\},$$

when $2p=24$ and terms a_{2p-n}, b_{2p-n}, etc. are accounted for above.

Ordinates were measured with a travelling microscope for five wave-forms at different points on the film and the mean ordinates were taken. This procedure took account of small variations in wave-form which sometimes occurred. Calculation showed that these variations were almost entirely due to small periodic amplitude-variations in the oscillator outputs.

§ 10. DISCUSSION OF RESULTS

The curves for which results are calculated for frequencies 250 and 500 c./sec. are shown in figure 5.

(*a*) and (*b*) show variation with volume at constant distance. Analysis gives

$$(a)\quad y_1 = 1{\cdot}12\cos\omega t + 1{\cdot}53\cos(2\omega t - 8{\cdot}1^\circ) + \ldots\ldots,$$
$$(b)\quad y_2 = 2{\cdot}00\cos\omega t + 2{\cdot}43\cos(2\omega t + 6{\cdot}9^\circ) + \ldots\ldots.$$

This gives a phase-change of 15·0° with the same variation of volume emitted as is used on a distance effect (i.e. at constant volume received).

(*c*) and (*d*) show traces for near and distant positions respectively:

$$(c)\quad y_3 = 1{\cdot}42\cos\omega t + 1{\cdot}33\cos(2\omega t + 69{\cdot}1^\circ) + \ldots\ldots,$$
$$(d)\quad y_4 = 1{\cdot}65\cos\omega t + 1{\cdot}67\cos(2\omega t + 86{\cdot}8^\circ) + \ldots\ldots.$$

(*c*) and (*d*) have a phase-difference of 17·7°, leaving 2·7° unaccounted for by change in volume-control.

From a previous calculation we have phase-change θ for a velocity difference 1 in 1000:

$$\theta = \frac{0{\cdot}36nfx}{c_1}.$$

Substituting $x=250$ cm. for all cases, and $n=2$, $f=250$, we have $\theta=1{\cdot}4^\circ$. Therefore velocities at frequencies 250 and 500 c./sec. do not differ by more than 1 in 500.

Traces for 250 and 750 c./sec. give

$$(a)\quad y_1 = 1{\cdot}15\cos\omega t + 0{\cdot}73\cos(3\omega t - 114{\cdot}5^\circ) + \ldots\ldots,$$
$$(b)\quad y_2 = 2{\cdot}76\cos\omega t + 1{\cdot}26\cos(3\omega t - 107{\cdot}8^\circ) + \ldots\ldots,$$
$$(c)\quad y_3 = 1{\cdot}62\cos\omega t + 1{\cdot}03\cos(3\omega t - 40{\cdot}2^\circ) + \ldots\ldots,$$
$$(d)\quad y_4 = 1{\cdot}86\cos\omega t + 0{\cdot}91\cos(3\omega t - 30{\cdot}8^\circ) + \ldots\ldots.$$

These give a phase-change of 2·7°, which corresponds to a velocity-difference of 1 in 750.

(*c*) and (*d*) repeated give

$$(c') \quad y_3 = 1{\cdot}66 \cos \omega t + 1{\cdot}64 \cos (3\omega t - 75{\cdot}8°) + \ldots\ldots,$$
$$(d') \quad y_4 = 1{\cdot}33 \cos \omega t + 1{\cdot}16 \cos (3\omega t - 66{\cdot}2°) + \ldots\ldots.$$

These again give a velocity-difference of 1 in 750 between frequencies 250 and 750 c./sec.

As a matter of interest the small 2nd harmonics of (*a*), (*b*), (*c'*) and (*d'*) above were determined. These gave a velocity-difference between 250 and 500 c./sec. of 1 in 450.

The curves for 500 and 1000 c./sec. give a phase-change corresponding to a velocity-difference of 1 in 1000.

It was pointed out when the analysis was discussed that its accuracy depended on the amplitudes of high harmonics being small. To confirm this the 12th harmonic was calculated for various cases:

250 and 500 c./sec., near position: $a_1 = 1{\cdot}42$; $a_{12} = 0{\cdot}0003$.
250 and 750 c./sec., distant position: $a_1 = 1{\cdot}86$; $a_{12} = 0{\cdot}0007$.
500 and 1000 c./sec., large amplitude: $a_1 = 2{\cdot}94$; $a_{12} = 0{\cdot}0002$.

We can be certain that for these curves $a_{21} \ll a_{12}$, so that the assumption as to accuracy of the analysis is justified. The results obtained are given in table 2.

Table 2

Fundamental frequency (c./sec.)	Harmonic frequency (c./sec.)	Upper limit to velocity-difference (parts per 1000)
250	500	2·0
250	500	2·2
250	750	1·3
250	750	1·3
500	1000	1·0

It is not suggested that the above velocity-differences are real ones. The fact that these differences all have the same sign, i.e. are positive with increasing frequency, suggests that they are due to some factor in the experiment not taken into account. They may be due to interaction between source and receiver, which varies with distance, or to a phase-displacement which varies with amplitude in the receiver itself.

§ 11. CONCLUSION

Changes in the phase-velocity of sound in air with frequency have been determined by a direct method which is independent of the temperature and humidity of the air. The results tabulated above show that between frequencies 250 and 1000 c./sec. the velocity does not vary by more than 3 parts in 1000, and between frequencies 500 and 1000 c./sec. not by more than 1 part in 1000.

§ 12. ACKNOWLEDGEMENT

It gives me much pleasure to express my thanks to Prof. E. N. da C. Andrade for suggesting the problem to me, and for valuable assistance and advice during the work.

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DISCUSSION

Prof. E. N. DA C. ANDRADE. The reason that I suggested to the author that he should investigate the constancy of the velocity of sound at sonic frequencies was that Dr D. H. Smith and I, using a tube method, particulars of which will be published shortly, found in our first experiments a well-marked variation of velocity with frequency in the region 600 to 1200 c./sec. Remarkably enough, the values found by Grüneisen and Merkel, which fall in the region 1400 to 5000 c./sec., showed a variation which exactly fitted on to the curve expressing our results. Although we have since convinced ourselves that, as would be expected, this apparent variation of velocity is due to some feature of the tube method as generally applied, it seemed worth while to attempt to establish the constancy beyond doubt, especially as few reliable measurements of velocity appeared at the time to have been made at frequencies below 1200 or so. I hope that Dr Walch's work will lead in due course to the vanishing of the unconvincing band-heard-at-a-distance argument from our text-books.

Dr J. E. R. CONSTABLE said that in Germany speech from a loud-speaker had been found to be intelligible five miles away. This constituted a more delicate test than that afforded by orchestral music, which was mentioned in the introductory section of the paper.

Mr T. B. VINYCOMB. Some years ago the B.T.H. Co. arranged a number of loud-speakers in a regular pattern on a high wall. I believe the object was to investigate whether distortion was introduced at great sound-intensities. They found that speech was clear and intelligible at distances of a couple of miles.

AUTHOR's reply. The details given by Dr J. E. R. Constable and Mr T. B. Vinycomb regarding the intelligibility of speech sounds at great distances are of interest and certainly constitute a more exact test than the one quoted from the elementary text-books. I am not aware, however, of any results which might be used to calculate how intelligibility would vary with dispersion of sound.

534.833.1

VIBRATION OF A BUILDING PARTITION AT AUDIO FREQUENCIES

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Received August 6, 1936. *Read October* 9, 1936

ABSTRACT. A simple device for observing the vibration of a partition has been used for determining the resonance frequencies and associated resistance coefficients of a sheet of window glass.

§ 1. INTRODUCTION

It has been shown[1,2,3,4,5,6] that there is a well-marked correlation between the sound-insulation and the weight per square foot of single sheets of widely varying material. Such a correlation would be expected if a simple partition could be regarded as a piston having elastic constraints so feeble that all its resonances were low compared with the lowest frequency at which measurements are made. The insulation calculated on this basis is, however, rather higher than the experimental figure, the difference increasing with the weight of the partition. Davis and Sabine explain this difference as due to the fact that partitions actually have resonances within the range of frequencies used for measurements. Davis also remarks that a series of resonances is necessary to account for the results.

It is of course to be expected that partitions will resonate at a number of frequencies, though these cannot be accurately calculated since the boundary conditions at the edge are so vague. It is therefore of interest to investigate them experimentally. It is difficult to deduce the resonance frequencies from measurements of the sound-transmission since pure tones would obviously be necessary, and errors would arise from interference effects. Accordingly the amplitude of the partition itself must be measured. E. Meyer[5] and A. H. Davis and T. S. Littler[7] have done this in the case of a brick wall and a building board respectively. Their measurements were, however, made at a set of selected frequencies and hence would not be expected to detect all the resonances of the wall.

In the following paper measurements made upon a sheet of window glass are described, the vibration being detected by an electromagnetic device. In contrast to the above-mentioned measurements, the frequency was varied continuously, its coincidence with a resonance frequency being shown by a sharp increase in the vibration of the glass.

§ 2. EXPERIMENTAL DETAILS

The measurements were made in the National Physical Laboratory's sound-absorbent transmission rooms. A sheet of 21-oz. glass measuring about 4 ft. by 4 ft. was clamped and sealed into the aperture which connects the two rooms and

was excited by pure tones from a loud-speaker directed obliquely towards it. Stationary-wave effects were minimized by the sound-absorbent character of the walls of the room.

To detect the vibration of the glass, light rectangular search coils constructed as in figures 1 *a* and 1 *b* were cemented to it. Attached to the centre of the sheet, coil *A* detects the majority of the resonances. There remain however a few resonances which have nodal lines passing through or near the point of the attachment. These can be detected by replacing coil *A* by coil *B*, used with its plane successively in two directions at right angles. The coils were rectangular in shape and each consisted of about 20 turns of fine insulated copper wire, wound as shown on a small piece of thin cardboard; they were too light to affect the vibrations of the glass appreciably. One side of each coil moved across the field of a permanent magnet, the pole pieces of which had an area of about $0{\cdot}75 \times 0{\cdot}75$ cm. The opposite side of the coil was well removed from the magnetic field. The voltages induced in the wire by its motion were detected after amplification by means of a copper-oxide rectifier and

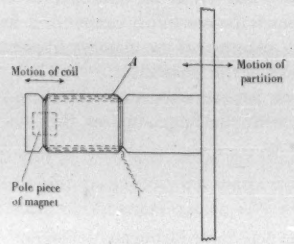

Figure 1 *a*.

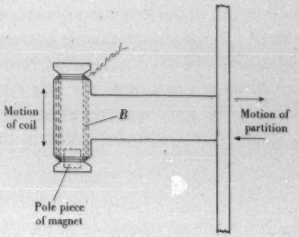

Figure 1 *b*.

galvanometer. To measure the output from the coil a comparison method was used, the e.m.f. from the secondary of a variable mutual inductance being substituted for the coil output. The coils were found to be sufficiently sensitive for examining the resonances of glass $\frac{1}{10}$ in. thick. By increasing the number of turns and the magnetic field, the sensitivity could no doubt be increased sufficiently for much heavier partitions to be dealt with. As the coils move in an approximately uniform magnetic field, their output is closely proportional to the amplitude of vibration. This property was used in determining the damping coefficients of the glass.

The resonance frequencies were determined very simply by varying the frequency of the loud-speaker note until the galvanometer deflection was a maximum. The frequency was then measured with a Dye sonometer[8]. For the most part the damping coefficients were determined from the frequency-changes, which reduced the amplitude as measured with the above described device to $\frac{3}{4}$ and $\frac{1}{2}$ of the resonance amplitude. In one or two cases, however, a complete resonance curve was drawn. At the low frequencies it was possible to obtain some check on the measurements by taking an oscillographic record of the decay of vibrations resulting from a blow. The search coil was in this case connected to the amplifier as before and the

amplifier output was connected to a Duddell oscillograph. Satisfactory agreement was found between the two measurements.

Errors in the measurements arise from the residual interference wave pattern in the room and the fact that the loud-speaker itself has resonances. The former effect is not likely to be noticeable except at low frequencies, since at other frequencies there would always be a number of nodes in the sound-field distributed over the surface of the glass, and change of frequency would only move some nodes on and a similar set of nodes off. The effect is in any case likely to be small owing to the absorbent character of the rooms. The fact that the same results were obtained when the loud-speaker was moved indicates that this source of error may be neglected.

Spurious peaks introduced by loud-speaker resonances are unlikely to have had much effect since roughly speaking the resonance peaks were 10 to 20 db. above the average vibration of the sheet, and of the loud-speaker resonances only the fundamental, at about 40 c./sec., was as large as this. In view of the non-resonant character of the cardboard used for the vibration-detector and the fact that its fundamental resonance was obviously very low, it is unlikely that any of the observed resonances had their origin in the detecting system, although the possibility cannot be definitely discounted. It appears justifiable however to assume that the majority, if not all, of the resonances observed were truly resonances of the glass sheet.

The stronger resonances and the vibration pattern associated with them could be observed by touching the glass lightly with the finger-tips or the knuckles. Nodes could very readily be traced in this way.

§ 3. RESULTS

The fundamental resonance of the glass as determined from an oscillogram of its vibration was 17 c./sec. This compares with the 17-c./sec. fundamental frequency calculated from Rayleigh's formula[9] for a circular plate with fixed edges, the same physical constants, and a diameter equal to a side of the square sheet of glass. Incidentally, the frequencies of the first ten overtones of such a disc coincided within 1 per cent with observed resonances of the glass sheet. The author is unable to say how much significance can be attached to this agreement, however.

About 95 well-marked resonance frequencies were observed below 3000 c./sec. Above this frequency the response had become so small that resonances could not be located with any accuracy. Plotted on a logarithmic scale the frequencies were approximately equally spaced, the geometric mean ratio between successive resonance frequencies being 1·055 : 1.

In the table are given the frequencies, resistance coefficients and sharpness of resonance of a number of the resonances observed.* These are selected on account of the large amplitudes associated with them.†

* The resistance coefficient given is the factor k in the equation of motion:

$$\ddot{x}+k\dot{x}+n^2x=0,$$

and the sharpness of resonance is $2n/k$, the reciprocal of the logarithmic decrement.

† It cannot, however, be inferred that these were the principal resonances, since the position of the search coil must have been more favourable to some resonances than to others.

Table. Frequency, resistance coefficient and sharpness of resonance of some resonances of a sheet of 21-oz. window glass measuring 4 ft. by 4 ft.

Resonance frequency (c./sec.)	Resistance coefficient (c.g.s. units)	Sharpness of resonance (c.g.s. units)
17	5·3*	40
72·5	6·9*	132
96	6·9	75
107	13·1	93
136	10·9	156
157	38	52
164	14	147
240	25	120
293	43	85
708	93	96
737	130	71
817	146	70
869	173	63
2635	570	58
3240	600	68

* These damping factors were determined both from the resonance curves and from oscillograms. Satisfactory agreement was found and the figures given are the means of the two results.

§ 4. DISCUSSION OF RESULTS

It will be seen that while the general trend is for the resistance coefficient to increase with frequency, the sharpness of the resonance and hence the logarithmic decrement nevertheless remain of the same order throughout. It may be observed in this connection that as the vibration pattern becomes more complex so the internal damping may be expected to increase. On the other hand the damping due to sound-radiation may be expected to decrease, since a partition divided into a number of areas vibrating in opposite phase is an inefficient sound-radiator[15b].

The radiation damping may be calculated approximately for the 17-cycle fundamental resonance since all parts of the sheet are in that instance in the same phase. The wave-length of the sound of the frequency in question is about 66 ft. and is therefore large compared with the sheet, which measured 4 ft. by 4 ft. Regarding the sheet of glass fixed in the transmission-room aperture as a circular rigid piston, of diameter equal to the side of the sheet and moving in a baffle, we have that the total radiation of energy from both sides is $a^2\rho\omega^2\dot{x}^2/c$ per unit area, where ρ is the density of air, c the velocity of sound in air, ω the pulsatance of the sound radiated, $\dot{x}$ the velocity of the piston's motion, and $2a$ the length of the side of the sheet. The mean rate of energy-radiation per unit area is accordingly $a^2\omega^2\rho\dot{x}_m^2/2c$, where $\dot{x}_m$ is the velocity amplitude. On substitution of numerical values, this gives

$$0{\cdot}9 \times \dot{x}_m^2 \text{ erg/cm}^2\text{-sec.}$$

The equation of motion of the sheet of glass can be written as $m\ddot{x} + k\dot{x} + n^2x = 0$, the average rate of energy dissipation being $\frac{1}{2}k\dot{x}_m^2$. Hence the resistance coefficient due to radiation is 1·8/0·68 or 2·6, since the glass weighed 0·68 g./cm.^{2}

This figure is about half the observed figure, 5·3, and is of interest as showing the large part played at the fundamental resonance by radiation damping. It does not appear to be possible to calculate the damping associated with the other modes of vibration.

§ 5. ACKNOWLEDGEMENTS

The author expresses his gratitude to Dr G. W. C. Kaye, Superintendent of the Physics Department, National Physical Laboratory, for his interest in this work and to Dr A. H. Davis for helpful criticism.

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DISCUSSION

For the discussion see p. 922.

534.833.1

THE VIBRATION PATTERN OF A WALL TRANSMITTING SOUND

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AND

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ABSTRACT. The vibration pattern of a 9-in. brick wall transmitting pure and warble notes of various frequencies has been determined by exploring the surface of the wall with an electromagnetic device. The pattern increases in complexity with increase of frequency. The effect of a warble tone is to decrease the difference between the greatest and least vibration energies.

Measurements made in a number of laboratories[1,2,3,4,5,6,7,8] have confirmed the existence of a correlation between the weight of a single homogeneous partition and its sound-insulating value. In fact if the sound insulation is measured logarithmically (e.g. in decibels) the relation between sound-insulation and the logarithm of the mass per square foot is very nearly linear.

Several attempts have been made to calculate the sound-insulation of a simple partition[1,9,10] but the formulae obtained, while they agree with experiment for light-weight partitions such as plywood and building board, give values for heavy partitions which are too high. Davis[1] points out that this can be explained by the resonant properties of such a partition but finds that more than one resonance is necessary to account for the discrepancy. The existence of a number of resonance frequencies for partitions has already been confirmed[11,12]. This is to be expected, of course, if the partition can be regarded as a vibrating plate clamped at the edges. One would expect the partition to have a series of nodal lines similar to Chladni's figures. It is in fact possible, if a thin partition such as a sheet of glass is vibrating at a resonance frequency, to trace the vibration pattern with one's finger-tips.

It is of interest to attempt to trace the vibration pattern of a thick wall under the conditions which obtain when its insulation is measured. A brick wall 9 in. thick, plastered on both faces and built into the test aperture in the large sound-transmission rooms[13] at the National Physical Laboratory, was used for this purpose. The wall had an area of about 10 ft. by 8 ft. Sound was generated in the room on one side of the wall, and on the other side the amplitude of vibration of the wall was measured at a number of positions distributed over its surface. To measure the amplitude a heavy moving-coil loud-speaker movement was used, a brass rod attached to the moving coil being pressed against the wall. The alternating voltage

induced in the moving coil by the vibrations conveyed to it via the brass rod was measured with a calibrated amplifier.

Measurements were made at frequencies of 100, 200, 300, 500, 700, 1000, 1600, 2000 and 4000 c./sec. At each frequency both a pure note and a warble note were used, the frequency in the latter case varying cyclically by ± 20 per cent up to 1000 cycles and thereafter by ± 100 cycles. As a change of the test frequency would be expected to alter the vibration pattern, special care was taken to maintain the frequency constant. A heterodyne oscillator having good frequency-stability was used, the frequency-drift being not greater than about one cycle per hour, and the frequency was rechecked at intervals of about 10 minutes. It was probably maintained constant during the measurements to about $\frac{1}{5}$ c./sec. The adequacy of these arrangements was confirmed by the fact that measurements made at the same test frequency on different days agreed closely.

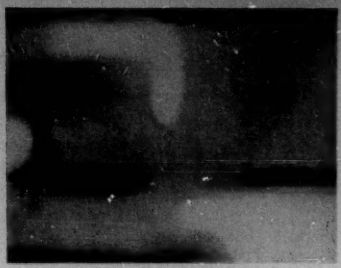
The number of observation points should obviously be as great as possible, but considerations of the labour involved limited the measurements to 63 points separated by 1 foot over a rectangle measuring 8 ft. $\times$ 6 ft. The need for measurements near the edge of the wall, where conditions are somewhat indefinite, was thus avoided. From the measurements obtained, contour maps were sketched, neighbouring contour lines corresponding to differences of 5 db. in the energy of wall-vibration. A selection from the figures thus obtained is reproduced in figures 1 and 2, in which the areas between the contours are shaded, the darker shading signifying the strongest vibration. The figures are arranged in pairs showing the vibration pattern with pure and warble tones respectively.

The fundamental frequency of the wall, as determined from a record of its free vibrations, was about 65 c./sec. This is outside the range of the frequencies used for the measurements.

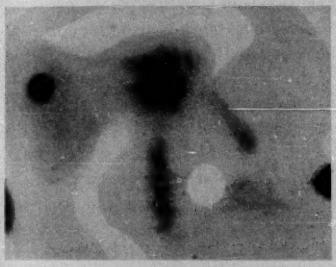
It will be noticed that a pattern is visible in all cases, though the patterns do not exhibit the symmetry of Chladni's figures. Three factors may be responsible for the lack of symmetry, viz. the indefinite conditions at the boundaries of the wall, the inhomogeneous nature of the wall, and the existence of interference patterns in the air-borne sound which excites the wall. Owing to the last-mentioned factor, the sound pressure over the wall will vary from point to point and might give rise to areas of minimum vibration on its own account.

The maxima and minima are well marked whether a pure or a warble tone is used. For pure notes the difference between the greatest and least vibration-energies is 12 db. at 100 c./sec., 34 db. at 500 c./sec., 35 db. at 1600 c./sec. and 22 db. at 4000 c./sec. The differences were somewhat less when a warble tone was used, being 13 db. at 100 c./sec., 12 db. at 500 c./sec., 21 db. at 1600 c./sec. and 16 db. at 4000 c./sec. In the corresponding case of the interference pattern in the air-borne sound in the room, with pure notes the maximum energy-differences were 9 db. at 100 c./sec. and 19 db. at 4000 c./sec., whereas with warble notes the differences were reduced to 2 db. at 100 c./sec. and 3 db. at 4000 c./sec. It appears therefore that the patterns observed on the wall are not greatly influenced by interference patterns in the air-borne sound which drives the wall.

100 *c./sec., pure tone*



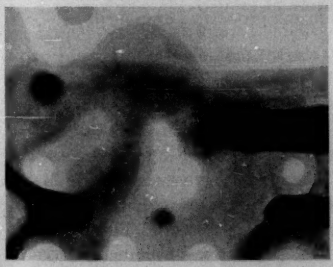
100 *c./sec., warble tone*



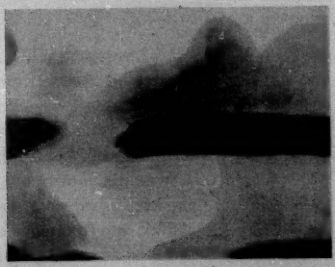
500 *c./sec., pure tone*

500 *c./sec., warble tone*

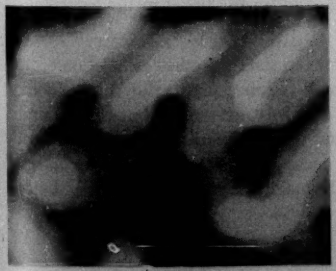
Figure 1. Vibration pattern of plastered 9-in. brick wall at frequencies of 100 and 500 c./sec. Areas of greatest vibration are shown black.



1600 *c./sec., pure tone*



1600 *c./sec., warble tone*



4000 *c./sec., pure tone*

4000 *c./sec., warble tone*

Figure 2. Vibration pattern of plastered 9-in. brick wall at frequencies of 1600 and 4000 c./sec. Areas of greatest vibration are shown black.

The authors express their gratitude to Dr G. W. C. Kaye, Superintendent of the Physics Department, and to Dr A. H. Davis for their interest in this work, to Messrs R. Berry and W. C. Copeland, who assisted with the measurements, and to Miss V. M. Fox, who prepared the figures.

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DISCUSSION ON THE PRECEDING TWO PAPERS

Mr T. Smith. Does the indefiniteness in the boundary conditions which prevents mathematical solution affect the general applicability of the experimental findings: that is, to what extent does variation in the constraints imposed at the edges of a block produce significant changes in the properties examined?

Prof. E. N. da C. Andrade. What exactly was the method of clamping adopted, and could consistent values be obtained if the plate was dismounted and then reclamped? I am particularly interested to note the large number of resonances, at more or less equal spacing on a logarithmic scale, found by Dr Constable. When carrying out experiments on a sensitive water-into-water jet, subjected to sound waves over a very wide range of frequency, I observed selective response at a large number of frequencies, spaced more or less as those described by him. The lowest response was, however, at a frequency of a few vibrations a second. This behaviour was originally attributed to some property of the jet, but was eventually traced to resonant response of the structure of the room. I attributed it mainly to resonances of the floor, and Dr Constable's experiments confirm my belief in the correctness of this attribution.

Dr L. E. C. Hughes. The discrepancy between the theoretical calculation of the loss through a partition, based on its mass, and the measured value might be explained by the wave transmission of energy which is not reflected at the incident surface on account of change of impedance and which accordingly generates sound on the far side apart from the motion of the mass as a whole, and thereby gives a diminished loss. Have the authors calculated the magnitude of the wave-transmission component?

In the technical application of springs for reducing the force applied to foundations arising from unbalanced forces within an engine, it is found that the low damping in the material of the spring permits the wave transmission of high-frequency components, although the spring is adequate for attenuating the forces of low frequency. To obviate this difficulty, damping-pads of cork or felt are used in addition to the springs, so that both high and low frequencies are catered for.

AUTHORS' reply. In reply to Mr T. Smith: The boundary conditions at the edge of a wall are in practice vague. The edges of the wall are not stationary, as can be shown by experiment; the other walls of the building which meet its edges are, in fact, not sufficiently rigid or massive to give a perfect clamped edge. Experiment also indicates, however, that the wall does not behave as if its edges were free. Accordingly, to calculate the resonance frequencies of such a wall is likely to be difficult. The problem is complicated by the lack of homogeneity of the wall. This makes it unlikely that the vibration patterns illustrated in this paper would repeat exactly for another wall built to the same specifications.

In reply to Prof. Andrade: Satisfactorily consistent results were obtained when the plate was dismounted and reclamped. The fundamental frequency of the glass sheet was 17 c./sec. The resonances above this frequency commenced at 26 c./sec. and thereafter increased in frequency by an average ratio of 1·055 : 1. The clamping was intended to imitate the conditions under which a sheet of glass is held in a window frame. For this reason the glass was plasticened to a wooden frame and the whole was clamped against the iron reveal of the sound transmission test aperture. The behaviour of the vibrating jet to which Prof. Andrade referred is very interesting. The resonances which affect it might be either those of the walls of the room (which usually range from 50 cycles upwards) or of the air, which embrace roughly speaking the same frequency range. We suggest that the latter is more probable.

In reply to Dr Hughes: The sound transmitted as wave motion through a partition was calculated by Rayleigh. The result coincides with that obtained for a rigid piston provided the piston is regarded as thin in comparison with the wavelength, i.e. that both faces of the piston are in the same phase. This form of transmission is, however, of minor importance since the critical angle for brickwork is of the order of 5°.

OBITUARY NOTICES

SIR JOHN CUNNINGHAM McLENNAN, K.B.E., F.R.S.

By JOHN SATTERLY

J. C. McLennan was born at Ingersoll, Ontario, Canada, on April 14, 1867 of Scottish parents. His early education was received in the schools of Ontario and at the University of Toronto, where he graduated in the mathematics and physics course in 1892. Appointed as an assistant in the department of physics, he soon forged ahead. Of a very energetic nature, he was responsible for the beginning of more than one university organization. He collected funds for the construction of the Convocation Hall of the University of Toronto, founded, with others, the Alumni Society, and started the undergraduate student newspaper.

He soon became widely known throughout Ontario as one of the leading scientists in the province. Quite early he showed his interest in research. He was one of the first in Canada to take X-ray photographs, he spent a year on his own financing at the Cavendish Laboratory, and later on journeyed to Germany. Returning to Toronto, he became professor of physics in 1904, was largely responsible for the building of the new physics laboratory, and became its director in 1907. The physics laboratory in Toronto was very generously planned, though not as completely as he had intended. His foresight was well exemplified in the organization of the building, and it has served well the needs of students and research workers up to the present time, when once more Toronto finds that an additional building is necessary if it is to maintain its front rank in the teaching of physics and in modern physical research. By practically allocating different floors to different colleagues, each in charge of some particular branch of physics, he encouraged each associate to build up his laboratory in his own way and to take a pride in it. In this way McLennan was released from the innumerable details of routine that sometimes nearly break the hearts of laboratory teachers.

His research work was interesting and many-sided. He had the intuition to judge what line of research was most promising and offered the better plums, and threw himself into it with great vigour. He was a born organizer and administrator, and he would collect a number of promising young men and, never stinting himself, he would drive them also as hard as they could go. The University of Toronto ably helped him with funds for the necessary apparatus, and he got his outside friends and wealthy organizations to supplement the university grants; the modern system of research scholarships and fellowships brought him the men.

In his early days he practically worked night as well as day, and although, as has been mentioned above, he worked his research men hard, they rarely regretted it, for he remembered them when they left, and many now hold university and other public posts which they owe largely to his enthusiasm on their behalf.

McLennan's earliest work was on gaseous ionization and radio-activity, and particularly on penetrating radiation, which he studied for many years, carrying out experiments on the ice of Lake Ontario in weather sometimes below zero. This work was followed by many years of spectroscopic research. Hilger's found him a good customer, and his beautiful papers enhanced the firm's reputation for accurate graphs. He and his co-workers wrote many papers on line spectra and spectrum series, on the spectra of gases in different states, and on ionization potentials. One particular research which brought him into prominent notice was that on the origin of the bright green line in the spectra of the aurora and the night sky. His explanation of this line excited much controversy, but was substantially correct. His views were well stated in the Bakerian Lecture to the Royal Society in 1928 on "The Aurora and its Spectrum".

An interlude in his spectroscopic researches occurred during the great war. In 1917 he was asked by the Admiralty to make a survey of Canada and look for helium in the natural gases—the helium was to be used because of its non-inflammability in balloons at the Front. The survey being completed and the results communicated to the Admiralty, he decided to go over to England and offer his services to that body on all scientific matters coming within its ambit. He pushed the project for the manufacture of helium, and his colleagues left in Toronto established factories in Hamilton and Calgary, and before the end of the war helium was actually produced and compressed in cylinders for shipment. But the Admiralty was parsimonious, and the United States having come into the war, the same project was pushed by them with such great vigour and enormous success that the centre of helium-production was shifted thither, and before the war was over supplies of helium from Texas were on their way to England.

Meanwhile McLennan and a band of workers which had gradually filtered over to him from Toronto and elsewhere were engaged on other problems, one of the chief being that of the detection and elimination of submarines. McLennan's pushfulness and disregard for red tape must have often surprised the routine-ridden officials at the Admiralty, but he found a great admirer—the admiration was mutual—in Sir John Fisher, and between them McLennan's work gave very satisfactory results. In fact, McLennan is often regarded in his homeland as the man who won the war. After the war he was invited to stay in England as scientific adviser to the Admiralty, but he preferred to be his own master, and that fact, combined with the love he bore his own university and laboratory, decided him to return to Toronto. Arriving back he found himself—again owing to his own foresight and energy—the possessor of a large quantity of helium. He himself tells how he found it just unloaded upon the docks at Liverpool and decided that it should return back across the Atlantic to the continent whence it had come, and he personally attended to its being put aboard the next west-bound steamer. Fired by the startling success of the work of Onnes at Leyden, he imitated Onnes, built a cryogenic plant in Toronto, again got a group of men at work and soon achieved success in this new field. He liquefied helium in 1923, and many in Toronto well remember his Royal Canadian Institute lecture in which he showed the Onnes experiment of the persistent current in the helium-

cooled lead ring, an experiment he was to repeat later to an admiring audience in the Royal Institution with helium dramatically brought to London by an aeroplane from Leyden.

McLennan was an ideal lecturer. He gave much consideration to what he had to say and said it well. His slides were always in order. He had a good presence and an engaging smile. He took his audience into his confidence and so carried them on that they thought they were part of him and carrying on the good work of research. He had a keen sense of the dramatic at lectures, especially public lectures. About 20 years ago he and his associates were measuring the residual ionization in gases. Lake Ontario is fairly free from radium, and to get rid of active impurities in the vessel containing the insulated rod whose electrical leak was being measured he made his ionization chamber of lake ice. To get rid of the effect of the penetrating radiation from the surroundings he sent his men to take the readings out on the ice in Toronto Bay on a night when the temperature was down near zero Fahrenheit. That night he was lecturing to the Royal Canadian Institute on residual ionization and penetrating radiation, and after a discussion of the issues involved he said "The men are down on the ice to-night. I expect their results at any minute." At that instant a knock occurred on the lecture-room door. The door being opened, in walked two men dressed as if for Arctic exploration. One of them silently handed McLennan a sheet of paper. There was a great hush, followed by a dramatic gesture from the Professor. "Ladies and Gentlemen, the ionization is down to 2·1 ions per c.c. per sec." Everybody in the room thought they had taken part in an important experiment, and the clapping was tumultuous.

McLennan was a great believer in educating the public in scientific matters and getting their support for scientific projects. Quite early elected a Fellow of the Royal Society of Canada (1903), he became later the President of the Mathematics, Physics and Chemistry Section (1910), President of the whole Society in 1924, and Flavelle Medallist in 1926. He was one of the strong men, and sometime president, of the Royal Canadian Institute in Toronto. He lectured up and down the country on the metric system. It was about the only thing he couldn't persuade the people to adopt. He was put on the Advisory Council for Scientific and Industrial Research in Canada in 1916 and did active work there until his retirement. He educated the country to give money to research and to become reconciled to the expenditures involved in a National Physical Laboratory and the scientific departments of the Government. He was responsible more than anyone else for the building of the large telescope at Victoria, B.C. By helping every other scientific worker, he prepared the way for their support when his own projects appeared. He was very much in demand as chairman, for he had an ideal way of presenting a subject and such was his good nature and forcefulness that few could withstand him when he got going. In his last few years in Toronto he became interested in the application of radium to the cure of cancer and was the most prominent member of the Ontario Commission which toured Europe and collected the necessary data for the report afterwards adopted and acted on by the provincial government.

He was a frequent visitor to the British Isles and the Continent. In his early

days he did this at some financial strain, but after his marriage things became easier and his annual trips brought him into contact with all the leading men of the sciences in which he was interested. He often spoke of the great kindness shown him by Professor Oliver Lodge on his first trip to England, and recurring visits enhanced his good opinion of England and Scotland. He spoke sometimes as if he were a native of Aberdeen. He was a regular attendant at the British Association and was largely responsible for raising the money and making such a success of the 1924 meeting in Toronto.

He delivered the Guthrie lecture to the Physical Society of London in 1918 on the origin of spectra. His Presidential Address to Section A of the British Association at Liverpool in 1923 was on the same subject, and many will remember the packed lecture hall and the admirable summary of the subject which he gave. In 1917 he was elected a Fellow of the Royal Society, but apparently it was not until 1925 that he became a Fellow of the Physical Society. As has been recorded above, he gave the Bakerian Lecture in 1928 on the aurora and its spectrum. The award of the Royal Medal in 1927 for his spectroscopic researches further increased his attachment to the old country. The physics department under his regime used books and apparatus made in the old country as much as possible. In 1931 he was made Dean of the School of Graduate Studies in the University of Toronto, but a year afterwards, largely owing to the ill-health of his wife during the Canadian winters, he resigned his positions as professor and dean and retired to England, where he built a house for himself at Virginia Water. But he could not remain inactive. A laboratory was furnished in his house and he was again soon at work.

Being so near London, he often attended the meetings of the Royal Society and was a regular frequenter of the Athenaeum. The Royal Society elected him to its Council, made him Vice-President, and trusted him, as an impartial visitor, to administer its scholarship funds, and as a man of means to attend on its behalf the many scientific conventions on the Continent where it was necessary to have a first-rate man to make clear the position of the Society and through it that of the British Government. He was a supporter of many societies doing public work, such as the Royal Society of Arts, and was in great demand as a lecturer on low temperatures and superconductivity. His Kelvin lecture to the Institution of Electrical Engineers was a notable achievement, and so was his address at the International Conference on Physics in 1934.

Following up his Ontario experience of work on the relief of cancer by the use of radium, he became in England the Director of the Cancer Research Hospital in Riding House Street. He was enthusiastic over the cure of pain, and thanks to his good relations with the Belgian Radium Company he became the temporary possessor of the largest single supply of radium, and was able to push forward the bomb method of radium treatment.

McLennan married in 1910 Elsie M. Ramsay, a native of Toronto of Scotch descent and at that time living at Bowland, Stow, near Galashiels. They formed a very happy pair; he could never do too much for her, and no doubt her kindness and advice and moderating influence were of the greatest service to him, for in his early life

he was impetuous and often said and did things on the spur of the moment that upset his opponents, whereas in his latter days he became milder and kinder. In a way, however, he never left off being a boy and was always happy when his old students crowded around him and they revived the memories of ancient fights.

Mrs McLennan died in 1933, and McLennan never recovered from his loss. When he returned to Toronto next spring in his capacity as visiting professor he gave to the physics department portraits of himself and his wife and made a most moving speech praising her virtues and all that she had been to him.

McLennan received many invitations to be professor elsewhere, and even to be chancellor of one University, but he preferred to stay in Toronto. He was the recipient of honorary degrees from Toronto, Manchester and Liverpool. It is no secret that he would have received a knighthood just after the war if the Canadian Government had not prohibited Canadians from being thus honoured by the King. As it was, it was not until after the embargo was lifted that the King was enabled to honour McLennan with a knighthood. Unfortunately McLennan did not long enjoy his honour, for although he was apparently in good health and attended the British Association at Norwich in September and a congress in Paris in October, he fell ill suddenly on the way back from Paris on October 9, and died before medical assistance could be obtained.

He will be long remembered. On his retirement from Toronto the University decided to name the laboratory in which he had done such good work the McLennan Laboratory. Many years ago his father-in-law endowed the Ramsay scholarship for the best student in practical physics. McLennan himself by his will has endowed another scholarship.

In Canada in general and in Ontario in particular his memory will be kept green by his old students, many of whom occupy important posts which they owe to his continued interest, by his colleagues, and by the great mass of people who for so long regarded him as one of themselves who had lifted himself up to do great things.

JOHN PARKE KIRKMAN

By C. W. HANSEL

Mr John Parke Kirkman died on December 15, 1935 in his 79th year. He was educated at Highgate School and Emmanuel College, Cambridge. He was a Scholar at King's College, London, before going to Cambridge. He had been a life member of the Physical Society since 1878. After a period as Headmaster of the Oxford Military College, he joined the Mathematical Staff of Bedford School in September 1893 and retired in July 1919. From his kindness of heart, discretion, and sanity of judgement, he exercised a beneficent influence not only in the form room but in the boarding house. For some years he was Principal of the Bedford Technical Institute and subsequently Chairman of its Executive Committee.

Few men have given more generously of their time and talents to the public service and particularly to the interests of scientific education than Mr Kirkman. He was a friend and admirer of the late Sir George Greenhill, and his outlook on mathematical teaching was essentially a practical one. He taught much of his mathematics in the laboratory and regarded practical mathematics as a laboratory subject which embraced all branches of practical science to which mathematics could be applied, such as practical physics, applied electricity, and engineering. He was untiring in his efforts to obtain laboratory accommodation and equipment not only in his own school, but in all schools.

It is impossible in this short notice to give an adequate idea of his work for the public service. He joined the Bedford Town Council in 1920. He was elected an Alderman and for a period acted as Deputy Mayor. He served as Chairman of the Housing Committee, Chairman of the Education Committee, and Vice-Chairman of the Public Health and Watch Committees. He was a member of the Bedfordshire Education Committee and served for a time as Chairman of the Higher Education Sub-Committee and Chairman of the Library Sub-Committee. He was appointed a Magistrate for the Borough of Bedford and for some years sat as Chairman of the local Juvenile Court.

He was appointed a Governor of the Harpur Trust by the Senate of Cambridge University. He was a member of the Estate and Finance Committee of the Harpur Trust and Chairman of several Harpur Trust Standing Sub-Committees. He acted as Chairman of the Schools Committee of the Harpur Trust.

Mr Kirkman was one of the founders of the Bedford Charity Organization Society. He was a life trustee of St John's Hospital Trust, and a trustee of the General Municipal Charities. He was a frequent, kindly, and sympathetic visitor to the old people in the Almshouses, and was a good friend to the Society for the Welfare of the Blind. There is no section of the community in Bedford that will not feel his loss.

SIR RICHARD TETLEY GLAZEBROOK

September 18, 1854—December 15, 1935

F.R.S., 1882; Assistant-director of the Cavendish Laboratory, 1891–8; Principal of University College, Liverpool, 1898–9; Director of the National Physical Laboratory, 1900–1919; President of the Physical Society, 1903–5; President of the Optical Society, 1904–5 and 1911–12; President of the Faraday Society, 1911–13; President of the Institute of Physics, 1919–21; President of the Institution of Electrical Engineers, 1906; Zaharoff Professor of Aviation and Director of the Aeronautical Department of the Imperial College of Science and Technology, 1920–3; Hughes Medal (Royal Society), 1909; Royal Medal (Royal Society), 1931; Foreign Secretary of the Royal Society, 1926–9; Gold Medal (Royal Society of Arts), 1917; Reid Lecturer, 1917; Guthrie Lecturer, 1931; Gold Medal (Royal Aeronautical Society), 1933; Knighthood, 1917; K.C.B., 1920; K.C.V.O., 1934.

The death of Sir Richard Glazebrook removes from our midst yet another of the slender band of veterans who came under the direct influence of Clerk

Maxwell, and who can tell us something of those early days when men plunged light-heartedly into exact physical research, their minds trained by the subtleties of the Mathematical Tripos, their hands by some practice at the bench of the village carpenter. Such was Glazebrook's training—and there is much to be said in its favour.

The son of a Liverpool doctor, he received his early education at Liverpool College, coming up to Trinity in 1872, shortly after Maxwell's appointment to the Cavendish Chair. It was a period of most active, and delightfully unsystematic work. Examinations under the new schedule, which recognized, tardily enough, the existence of such branches of science as Heat, Electricity and Magnetism, were instituted in 1873, and the Cavendish Laboratory (furnished, as Maxwell later optimistically remarked, "with all the instruments required in the present state of science") was opened in 1874. The shadow of Kelvin's quadrant electrometer loomed large in the physics of the seventies. We remember how Ramsay as a youngster at Glasgow was set, as his first exercise in practical physics, to taking the kinks out of a coil of copper wire, and then, having served this apprenticeship, was promoted to the study of the quadrant electrometer. So in this far-off Cambridge of sixty years since, we read (in tones slightly hushed) of the new Laboratory and "the Professor's private room, with the Quadrant Electrometer on a shelf in one corner".

Glazebrook himself, after graduating as fifth wrangler in the Tripos of 1876, went to the Cavendish Laboratory, on his tutor's suggestion, in search of a possible subject for a fellowship dissertation, and Maxwell set him to what we should nowadays regard as a very elementary piece of work, some Wheatstone's bridge measurements. Glazebrook has put on record his regret that he had not assimilated this knowledge earlier, for in the Tripos examination Rayleigh had set the question "Explain the Wheatstone's Bridge method of measuring resistances", and Glazebrook, fresh from the study of those portions of Maxwell's treatise which were *not* concerned with resistance measurement, found himself unable to touch both question and an easy rider appended thereto. After a little time spent on such measurements Glazebrook had to search for any possible variation in the electromotive forces of the Daniell's cells used by Chrystal in his experiments on the validity of Ohm's law, and the inevitable quadrant electrometer was pressed into service. Glazebrook, in common with most other physicists, found the instrument a trial, "perhaps a useful one", as he drily remarked. But measurements on Daniell's cells were not likely to lead to a fellowship dissertation, and Glazebrook found his subject in a careful and accurate test of Fresnel's wave surface in aragonite and in Iceland spar. The experimental work involved goniometric measurements of high precision, and was carried out under primitive and uncomfortable conditions. It shows that, taking into account the effects of dispersion, "Huygens' construction for the extraordinary wave-surface represents its true form to within about 1 in 30,000".

It is difficult in these days of organized laboratory classes of all grades and sizes to realize that systematic laboratory teaching, as we know it, is a product of the last

two generations. Rayleigh instituted practical classes in Cambridge with Glazebrook to assist in the organization of the system and with Napier Shaw as demonstrator. They started from "the foots", as the Lancashire phrase has it, and their experiences were remarkable enough. Was it about this time or a little later that there emerged the heroic figure of him who saw in a thermometer an instrument for the determination of specific gravities, though, as Wilberforce remarked in telling the story, "when furnished with a thermometer, a basin of water and a bit of string, he failed to achieve any numerical result"? At any rate, Glazebrook left his mark on the teaching in the laboratory, and the many editions of "Glazebrook and Shaw" testify to its almost world-wide influence. Of Glazebrook's other books his *Physical Optics*, now in a sense obsolete, is yet of value as giving a characteristically clear picture of the state of that science in the early eighties. His elementary text-books, the first editions of which are now some forty years old, still hold their own against more youthful competitors, and his biographical study of Clerk Maxwell contains one of the best summaries extant of Maxwell's teachings, and has, moreover, the advantage of having been written by one who had first-hand knowledge of his subject.

During this period Glazebrook's research work was moving in the direction of the tasks which dominated his later life, papers on optical subjects being more and more replaced by papers dealing with electrical standards and measurements. One of the earliest of these papers (1883) records an absolute determination of resistance by that method which consists in comparing the steady deflection, in a circuit possessing a mutual inductance which may be calculated accurately, with the inductive kick obtained on reversal of the battery current. The results of the investigation, reduced to their latest form, showed that

$$1 \text{ B.A. unit} = 0{\cdot}98665 \times 10^9 \text{ c.g.s. units.}$$

The series of such papers published previously to his appointment to the National Physical Laboratory ends with the investigation which describes the determination of v made in collaboration with Sir Oliver Lodge. In this determination, a parallel-plate condenser, whose capacity in electrostatic measure could be accurately calculated, was placed in an inductive circuit of negligible resistance, and the capacity in electromagnetic measure was deduced from observation of the period of the oscillatory discharge and a knowledge of the magnitude of the self-inductance. The spark discharge was photographed on a plate which rotated at a speed of about 80 revolutions per second, and the period was thus determined with considerable accuracy. The capacity of the inductance coils used was a source of much trouble, and the final result ($3{\cdot}009 \times 10^{10}$ cm. sec.$^{-1}$) was not regarded as one of exceedingly high precision. The method is, however, one of considerable physical interest, and may be profitably used in a laboratory determination of v.

In 1898 he left Cambridge, having in the interval become Assistant-Director of the Laboratory and Senior Bursar of Trinity, to take up the position of Principal of University College, Liverpool. He barely assumed these duties to leave them, for in 1900 there fell to him his life's major task—that of Director of the newly formed National Physical Laboratory.

Glazebrook left his mark on many things and many movements—perhaps it was because in most of them the work had to be started, very much *ab initio*. It was so in his fellowship work, when two years of optical measurements produced papers of major importance from one who, at the beginning of the period, knew nothing of the Wheatstone's bridge; so, in his teaching work in practical physics; so, in the newly formed National Physical Laboratory, where buildings had to be erected, a staff brought into being, and a plan of campaign drawn out. In nothing are Glazebrook's remarkable capacities as leader and administrator more clearly shown than in his work at the National Physical Laboratory. In 1902, the two departments of physics and engineering and a staff of thirty sufficed for its modest needs—needs which rapidly grew with Glazebrook's growing experience. Building after building rose near Bushy House; metrology, electrotechnics and photometry, chemistry and metallurgy, were insistent in their demands for housing adequate to their needs; and all the while the growing requirements of the two original departments called for expansion in their staff, equipment and in the space allotted to them. The year 1911 saw the opening of the gigantic tank for experiments on ship-models, and aeronautical research was begun in 1909. Withal, as was to be expected in one of Glazebrook's outlook, those activities which are concerned with the improvement of standards of measurement in all branches of science, were never in the slightest danger of relegation to a subsidiary position. Not to confuse the record by considering in detail the stimulus afforded by the War years, it is sufficient to note that in ten years from 1902, the two departments and staff of 30, had expanded to six departments and a personnel of 150.

This, more than any other of Glazebrook's many achievements, is his enduring memorial; and of Glazebrook and the National Physical Laboratory it may be said, as truly as of Wren and St Paul's—*Si monumentum requiris, circumspice*.

Glazebrook laid down his duties as Director in 1919. Retirement to him meant no more than a shifting of his activities, for his was not the type that retires to cultivate its garden. He was happy in the opportunity of his death, for he worked at full pressure until his last day. At various times during these later years he was Director of the Aeronautical Department of the Imperial College of Science and Technology, Editor of the *Dictionary of Applied Physics* and Chairman of the Symbols, Units and Nomenclature Commission of the International Union of Pure and Applied Physics. All this work was stamped with the impress of his strong personality. The *Dictionary*, in particular, shows how serenely he could ignore that which made no appeal to him; for the *Dictionary*, wide as is its scope, contains not even a passing mention of colloid physics. Work on electrical standards played a great part in his life; such work, exact, shining perhaps with a dry light, and calling for great precision and clarity in definition, made a strong appeal to him; no better illustration of Glazebrook's mind and his meticulous scholarship can be found than in his Guthrie Lecture of 1931 on "Standards of Measurement, their History and Development".

Glazebrook's was an outstanding figure in the history of the physics of the past sixty years. Competent, exact, completely and easily master of the tools of the

physicist's craft, absorbed in the day's work—these are the phrases that rise in the mind as one's thoughts travel back to the committee rooms of the Royal Society; as one pictures again the tall, spare figure of the octogenarian striding into the room with the activity of one of half his years; hears the precise and curiously clipped diction; and sees the steel spectacles removed with a sudden, almost nervous jerk, and used to emphasize a point in the argument. That is the milieu in which one almost automatically places Glazebrook. Striking as was his work in physics, he will be remembered longest as a pre-eminently successful administrator. As such he will live long in the affectionate memories of those who have served under him, and not least affectionately in the memories of some of those who, on occasion, differed from (and with) him.

A. F.

REVIEWS OF BOOKS

Energy and Matter, by CHARLES B. BAZZONI. *Space, Time and Relativity*, by H. HORTON SHELDON. (From The University Series, London: Messrs Chapman and Hall, Ltd.) Price of each volume 4*s*. 6*d*. net.

These two volumes are written with the purpose of presenting their respective subjects to readers who are not specialists but who seek a general acquaintance with the progress of modern physics.

The first volume traces the history of atomic theories, outlining the early views which prevailed before the discovery of the electron, and passing on to give, in approximately two-thirds of the volume, an account of the work of physicists since 1895. The author has produced a very interesting and a very readable work, and apart from providing the reader with accurate and plentiful detail he has succeeded in expressing the spirit of scientific research and the enthusiasm of the researcher. He discusses some of the changes in the point of view which most recent developments have brought in their train, and in a very short closing chapter he refers to comments of a metaphysical character which some modern writers have thought well to make, attaching to them just that quantum of importance which they deserve.

It is admittedly difficult to write a popular account of the theory of relativity, and the writer of the second of these volumes has set himself a difficult task in attempting to make clear to the layman the principles of Einstein's theory. Nevertheless he has succeeded in giving some idea of the viewpoint of the theory and of its important consequences. The illustration of the relativity of time, however interesting as a subject of thought, does not appear to have anything to do with the difficulty about simultaneity which the theory points out. Further, it is not worth while to bring into the discussion such abstruse questions as are involved in the theory of parallelism. Our chief adverse criticism is directed to the unscientific character of the work as a whole. It is as important to interpret the enthusiasm and the spirit of the scientific worker as to give the detail of his discoveries. The present work is too sensational. We are shown a page of an American newspaper with a few lines of one of Einstein's papers published in various forms and we are asked to marvel at the popular interest which made its publication good journalism. Again, in the illustration of the relativity of time the interstellar news delivered simultaneously everywhere is that of a murder. This sort of wonder is not the wonder of science. We are getting used to the complicated illustrations used by some writers and lecturers to convey an idea of the great magnitude of some of the numbers occurring in physics. This book is distinguished for the complexity and length of one of these in an attempt to show how large is the number 10^{63}. If the American layman, for whom this book is primarily written, speaks as the English think he does, one can imagine that after reading it he might say: "I guess this is some number", and that, being a complete, precise and concise statement of fact, is more true to the spirit of science than a whole page of rigmarole. We come to the end of the book with a feeling of disappointment that a branch of physics has been brought into contact with the advertisement page and the sensational columns of a second-rate newspaper.

H. T. F.

Anschauliche Quantentheorie, by Dr PASCUAL JORDAN. Pp. xii+320. (Berlin: Julius Springer, 1936.) RM. 12.

This volume gives an admirable descriptive summary of the principal results obtained by the modern quantum theory and a brief history of the early development of that theory. If there is one criticism which can be made of the book, it is that the author has attempted to cover rather too much ground. In fact, the book discusses the quantum theory from every aspect—experimental, mathematical and philosophical. The first chapter gives a summary of the physical background of quantum physics, emphasizing specially the duality of the corpuscular and undulatory concepts of matter and indicating the physical significance of stationary states and quantization. The second chapter provides a theoretical analysis of the fundamental experiments, and discusses in detail the applications of the correspondence principle and the calculation of probabilities of transition.

The mathematical scheme of contemporary quantum theory is developed in the third and fourth chapters. These give a condensed sketch of matrix mechanics and of wave mechanics in which most of the principal results are stated, although limitation of space has prevented more than very brief sketches of the methods of proof. The fourth chapter deals specially with problems in which many particles are involved and also discusses the application of the quantum theory to the elementary articles of microphysics, viz. the alpha particle, the spinning electron, the nucleus, and the neutrino. The concluding chapter gives a very interesting account of the philosophical background of the quantum theory, indicating its relations to the general method of positivism and to the fundamental questions of causality and finality. The whole of this treatise is most useful and valuable as a work of reference—indeed, it is primarily as a work of reference and a useful summary of the subject that it will most probably be used. It is therefore especially regrettable that no index is included.

G. T.

Foundations of Physics, by R. B. LINDSAY and H. MARGENAU. Pp. xiii+537. (New York: Wiley and Sons. London: Chapman and Hall, Ltd.) 22*s*. 6*d*.

This book covers so much ground that a list of chapter headings and lengths is perhaps the best way of indicating its scope. The list is as follows: I. The meaning of a physical theory. (58 pp.) II. Space and time in physics. (20 pp.) III. The foundations of mechanics. (80 pp.) IV. Probability and some of its applications. (29 pp.) V. The statistical point of view. (92 pp.) VI. The physics of continua. (39 pp.) VII. The electron theory and special relativity. (37 pp.) VIII. The general theory of relativity. (31 pp.) IX. Quantum mechanics. (128 pp.) X. The problem of causality. (14 pp.)

The treatment is unusual and interesting. Certain sections of theoretical physics have been selected, and very judiciously selected, largely on the basis of their suitability as "material for exemplifying the basic structure of physical thought". A very concise and more or less conventional and familiar mathematico-physical treatment of these sections makes up the skeleton of the book; this in itself constitutes a useful connected summary of a great deal of moderately advanced physics, but its function here is the ancillary one of providing the framework for a full discussion of the foundations of the theories expounded. In other words, and in brief, the book is much more concerned with epistemology than with details of the mathematical technique of theoretical physics.

"The authors would like to believe that, among other things, they have made clear, to put it crudely, how mathematics gets into physics and how, moreover, certain mathematical methods are peculiarly appropriate for particular physical theories." In this they have been conspicuously successful, and they are to be congratulated upon the production of an original and inspiring book.

It is to be hoped that this work will be very widely read; it can be cordially recommended to all senior students of physics, and it will make a special appeal to a great many teachers of the subject.

H. R. R.

Structure Factor Tables, by KATHLEEN LONSDALE. Pp. 181. (London: G. Bell and Sons, Ltd., for the Royal Institution, 1936.) 10*s*.

The full title of this book is "Simplified Structure Factor and Electron Density Formulae for the 230 space groups of mathematical crystallography." The aim of the author as stated in the foreword has been to present tables of structure factors in a practical form, suitable for direct use. They differ from the general structure-factor equations included in the *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, which cannot be applied without the further simplifications tabulated in this volume.

A full explanation of the way to use the formulae is contained in the introduction. The method adopted in the production of the volume, that of photographing the manuscript, precludes the possibility of printers' errors. The tables are clearly set out, are condensed to minimum space, and are easy to follow after a perusal of the directions which the author gives in the introduction.

The amount of work entailed in the preparation of the tables has been great. The author and the Royal Institution deserve the gratitude of all workers in X-ray crystal-analysis for preparing and publishing the tables so that they may be within reach of everyone interested in this important branch of modern physics. Every laboratory where work on crystal-analysis is being carried out should be in possession of this most valuable volume, which will undoubtedly be the means of curtailing much of the initial work necessary in problems involving structure factor and electron-density. And the price is exceedingly moderate.

E. A. O.

Heat for Advanced Students, by E. EDSER, revised by N. M. BLIGH. Pp. x+487. (London: Macmillan and Co.) 6*s*.

The question is not whether this is a good text-book of heat (that has been answered by its 37 years of life) but whether the revision by a hand other than that of its original author has been successful. Such a revision must be very difficult. On one side is Scylla, represented by the temptation to alter the book out of recognition in the effort to bring it up to date, and on the other Charybdis, or the spirit of reverence which forbids the reviser to alter that which the author wrote.

The additions are numerous and mainly helpful. One may cite in particular the paragraph on the change of density with temperature, and the new description of thermometer-calibration, but the chief one, the introduction to the quantum theory, is so compressed that it is doubtful whether students at the stage when they normally read Edser will carry away any understanding of the utility of the theory. They will certainly have a confused idea that Nernst's theorem is some sort of consequence of the theory. (Incidentally, the functional f which occurs on page 454 is almost enough to frighten the student off the subject; of all known symbols it most resembles Sommerfeld's sign for integration over a period.)

A certain number of wise deletions have taken place, but they are not sufficient, for it must be remembered that one of the outstanding features of Edser's book when it first appeared was the fact that it was so nearly abreast of the latest work. Had the author been writing it now, he would have described not Regnault's apparatus for vapour pressures at high temperatures but either that used at Munich or that used at Washington for the work on steam and carbon dioxide. He would also have described some more modern forms of thermal-conductivity apparatus, since they are actually easier to understand than the earlier forms.

Among omissions, we note the absence of any description of a total-radiation or an optical pyrometer, and the failure to make clear to the student that the Seebeck effect is

one which is widely used in factories and works for the measurement of temperature. There is no reference to the fact that the ventilated wet-bulb hygrometer exists.

Again (and it is to be remembered that all these complaints are only made because the book is so good that one expects to see many further editions, and wishes them to be even better), the numerical data nearly all need revision. On page 27 the boiling-points of water at different pressures are given to 0·0001° C., when the values differ by 0·004° from the recent results of Moser. On pages 239 and 464 we learn that the vapour pressure of steam at 40° C. is 54·87 mm. of mercury, whilst on page 353 it is 54·91, and in a second table on page 464 it is 55·55. The conductivity of aluminium on page 421 is wrong by about 50 per cent.

Finally, one may regret that one or two hoary old misstatements have been left uncorrected. Newton's law of cooling was never put forward as applying to radiation, as seems to be asserted on page 450, nor did Stefan say anything about black bodies when he announced his law. He deduced it, as stated, from observations by Dulong and Petit, on real bodies which were not in a black-body enclosure.

However long the above catalogue of blemishes may seem, it is to be taken, not as a sign of disapproval of the book, but rather as an indication that the latter is worthy of the most careful attention. Many a student will gain his first knowledge of the subject from it, and we all wish him to have a book as nearly perfect as possible. J. H. A.

Thermodynamics for Engineers, by the late Sir J. A. EWING. Pp. xv+389. 2nd ed. (Cambridge University Press.) 21*s*. net.

One of the outstanding characteristics of Sir Alfred Ewing was his lucid style of writing. He took meticulous care in the presentation of his material and his books are models of what scientific works should be as regards clarity of expression and literary style. Until the time of his death the revision of his book on thermodynamics had provided him with a congenial task which, alas, he was not destined to complete. Prof. Egerton has undertaken to complete the revision and readers will feel grateful to him for the care and thoroughness with which the work has been carried out. Prof. Egerton's work in connexion with the preparation of the steam tables brought him into close contact with Sir Alfred, so one has the assurance that the revision is in accordance with the author's views on the subject.

Sir Alfred had very decided preferences as regards the symbols for the thermodynamical quantities most used by engineers. The symbols he has adopted are in accord with those agreed by the International Union of Pure and Applied Physics, except that ψ has been used for free energy and F for electromotive force, while G (Gibbs's function) is taken as $-G$, the positive value being more convenient for users of steam tables.

A committee of the Physical, Chemical, and Faraday Societies is now at work considering the symbols for use in thermodynamics, and whilst they have not issued their final report it appears probable that the letter F will be used for free energy and that Greek letters will be avoided.

One minor point merits comment. It is stated on page 265 that "In triatomic gases it may be conjectured that the three atoms of any molecule group themselves not in one straight line—which would be an unstable arrangement—but so that the massive centres lie at the corners of a triangle". This statement needs modification, for it is now generally accepted that some triatomic gases, carbon dioxide for example, have a linear structure.

E. G.

A Laboratory Manual of Experiments in Physics, by L. R. INGERSOLL and M. J. MARTIN. Pp. ix+301. (London: The McGraw-Hill Publishing Co., Ltd.) 15*s*.

The course of experimental work covered in this manual is of the standard of the intermediate examinations in the British universities. The book, which has reached its fourth edition, was primarily written for the students in the University of Wisconsin, so that many of the experimental details, such as resistances to be unplugged, apply to the apparatus set out for the use of the students in the Wisconsin laboratories. The directions given are comprehensive, some pertinent questions are appended to each description of an experiment and, except in the case of the simple experiments in light, the student is told what curves he should plot. The experiments on mirrors and lenses are not at all good. For example, in the case of the concave mirror when the lamp is inside the principal focus, "have some one hold a pencil behind the mirror and then determine, by moving the head from side to side, when the image and the pencil appear to be at the same distance on the other side of the mirror".

The scientist has always given his work freely to the world, so that it is with regret that one reads the announcement that "this book, or parts thereof, may not be reproduced in any form without permission of the publishers". Of necessity in books of this kind "old songs turn up again". Presumably, therefore, it is the publisher who has to realize the fact, which must be known by each of the authors, that

> "When 'Omer smote 'is blooming lyre,
> He'd 'eard men sing by land an' sea;
> An' what 'e thought 'e might require,
> 'E went and took—the same as me."

J. H. B.

The Rational Quartic Curve in Space of Three and Four Dimensions, by H. G. TELLING. Pp. vi+78. (Number 34 of the Cambridge Tracts. Cambridge: The University Press.) 5*s*.

The subject of higher geometry is one which, as far as one can foresee, is never likely to have a direct bearing on or application to physics. It is really a means of expressing algebraic theorems succinctly, and with perhaps less of rigour or generality than the analyst would require. The present tract enters on the four-dimensional problem without any preliminaries, and then proceeds to the problem in three dimensions. The book is packed exceedingly full of results, and is in fact a marvel of compression which could hardly be read profitably without a particularly good knowledge of the subject as set out in the general treatises. The standard of printing is all that we have come to expect in books from the Cambridge Press, and the book is cheaper than any of its last twelve predecessors in the series of which it forms part. May we dare to hope that this heralds a gradual fall in the prices of mathematical works?

J. H. A.

The Scientist in Action, by WILLIAM H. GEORGE, M.Sc., Ph.D., F.Inst.P. Pp. 355. (London: Williams and Norgate, Ltd.) 10*s*. 6*d*. net.

This book is the result of an attempt by the author to clarify his mind on the relationship between experiment and theory and more especially on the relationship between experimental and mathematical physics, and can be recommended to those who wish to do likewise. In it he develops the theory of patterning which is similar to that adopted by Mach, Kirchhoff, Karl Pearson and Hobson and is in contradistinction to the theory of absolute truth or inner reality of science at present more widely used, especially by popular writers on scientific subjects. The author rejects the idea that "Science is based on measurement" in favour of the idea that "Science is based on fact, or human judgement

of coincidence". He says: "Traditionally, experiment and theory have always been linked by philosophy. I now see them as linked only by the human research worker. Logically, science is found to be inseparable from scientists, but quite separate from philosophy." And again: "Whilst the traditional way is to regard the facts of science as something like the parts of a jig-saw puzzle which can be fitted together in one and only one way, I regard them rather as the tiny pieces of a mosaic, which can be fitted together in many ways. A new theory in an old subject is for me a new mosaic pattern made with the pieces taken from an older pattern. To speak of the one as being right, and the other as wrong, is then as inappropriate to the scientific as to the artistic mosaic." Thus Dr George has abandoned the traditional view and treats scientific research as a problem in human action and the scientist merely as part of the paraphernalia of research. According to him the application of these ideas "is a way of explaining things without using the idea of cause.... The things here explained...are effects without any causes of the agent type."

The author makes some significant statements about the cost of research and estimates that the minimum average cost nowadays of a research paper covering one year's work is of the order of £500. Would it not be an excellent thing to bring this to the attention of all research workers, in the hope of concentrating the limited funds available for research upon problems which seem most important and fundamental, instead of on those which happen to be most convenient and suitable for the award of a higher degree?!

Dr George's process of "clarifying his mind" is reflected in the varying style of the book. Some passages are difficult and heavy, whilst in others the haze has evidently cleared and given place to bright sunshine with a consequent clear, jovial and altogether delightful style. He evinces a wide and intimate knowledge of everyday affairs, be it the child in the nursery, the technique of ballet, the thoughts of the ordinary post-graduate student, or the difficulties of driving a car in traffic and conducting an interesting conversation at the same time, all of which he uses in his mosaic pattern.

Dr George is Royal Society Sorby Research Fellow and an Honorary Lecturer in Physics in the University of Sheffield.

H. R. L.

Flame, by O. C. DE C. ELLIS and W. A. KIRKBY. Pp. vi + 106. (Methuen's Monographs on Chemical Subjects.) 3*s*.

The two authors are members of the staff of the Flame Section of the Safety in Mines Research Board and are therefore well qualified to deal with the topic under review. The book takes the reader from the familiar jet flame to the flame that spreads through a prepared mixture of mutually reactive gases, summarizing in a concise manner the theories that have been recently propounded to account for the observed phenomena. The reader wishing to have a rapid survey of recent advances in our knowledge of the aerodynamical and chemical aspects of combustion will find the little volume a mine of information.

E. G.

Controlled Humidity in Industry, by M. C. MARSH, M.A., Ph.D. Pp. 121 with 43 figures. (London: Charles Griffin.) 6*s*.

The object of this book is to review the question of the control of humidity under industrial conditions and the principles of the instruments and plants used for that purpose. The author deals in turn with the methods of measuring, of increasing and of decreasing humidity, air-conditioning plants, and automatic humidity-controls. The book should be of great service to manufacturers, engineers and research workers as it sets out what has been accomplished in the variation and control of humidity to meet the requirements of modern industrial processes. The author brings to bear on the subject an unbiassed mind and puts at the disposal of the public information gathered in the course of his work as member of the staff of the Wool Industries Research Association.

A feature of the book which deserves mention is the two appendices, one dealing with the application of factory and workshop acts to artificially humidified buildings and the other a list of manufacturers of plants and instruments for humidity-control.

E. G.

Electrical Engineering in Radiology, by L. G. H. SARSFIELD. Pp. 284. (London: Chapman and Hall, Ltd.) 25*s*. net.

The X-ray tube has now taken its place as a tool for technicians. Mr Sarsfield, speaking as an engineer, claims that "It is possible to take pride in the appearance and place confidence in the operation of modern X-ray gear, and this could certainly not have been said in the old days of noisy, inefficient inductance coils...primitive switch gear, and inadequate wiring", when it was only found in rooms "littered with odd pieces of ill-assorted apparatus joined together with various wires, some up in the air and some on the floor". Most physicists will appreciate the point, and should they wish to learn how this tidiness and efficiency may be achieved, this book will supply the information required. It treats of those portions of electrical engineering which have been applied to the development of X-ray technique. It is clearly written and includes quite recent developments, and all physicists who are concerned with large-scale investigations involving the generation, transmission and control of high voltages will find the book very helpful. Such questions as the design of transformers, insulating supports, terminals, and rectifiers are discussed, and there is much valuable advice based on the author's wide experience of this subject gained in the Research Department at Woolwich.

L. H.

The Penrose Annual Review of the Graphic Art, vol. 38, 1936. Edited by R. B. FISHENDEN. (London: Percy Lund Humphries and Co. Ltd.) 10*s*.

The volume under review marks the beginning of a new series in which the size has been increased to 11 by 8 in. The printing and illustrations are a sheer joy and one regrets that our scientific literature cannot be adorned occasionally by such magnificent examples of the block-maker's art. The volume contains a large number of general articles covering the field. These range from "The psychology of English and German posters" to "Electrical dot etching".

In the article by Major J. J. Kruger on photogravure in South Africa and in particular the printing of postage stamps, we are informed that the design of the current postage stamps for the South African Government was completed in Holland and printed on machines manufactured in Germany. It is claimed that as the result of such enterprise South Africa is the first member of the British Commonwealth of Nations to embark on printing its postage stamps in gravure.

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